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SIGNIFICANCE OF PARTICLE-SIZE FRACTIONS IN READILY SOLUBLE PHOSPHORUS EXTRACTIONS BY THE ACETIC, TRUOG, AND LACTATE METHODS

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CORRELATIONS between crop responses and readily soluble phosphorus by the acetic, Truog, and lactate methods for soils in north-east Scotland show that the usefulness of the values as criteria of phosphorus status depends on the nature of the soil parent material (Williams, Reith, and Inkson, 1952). Similarly, earlier work showed that redistribution of phosphorus occurs to varying extents during acetic-acid extractions of the different soil types (Williams, 1951). These findings, together with other considerations (Williams, 1952), suggested that the chemical significance of the values, particularly for the acetic method, varies for the different soils. The present investigation of profile samples of widely differing properties was undertaken to examine this question.

The main feature of the experimental approach is that the four particle-size fractions have been extracted individually and in combination to assess their significance in relation to the normal soil extractions. Simple dispersion in water proved highly effective, enabling large-scale separations of the fractions to be carried out with little loss of phosphorus and minimum disturbance of its natural distribution. The coarse-sand, fine-sand, and clay fractions were satisfactorily pure and representative, but the silt fractions were contaminated with clay. This does not materially affect the gross distribution of phosphorus, but it limits the significance of the results for the silt fractions extracted with weak agents.

Experimental

The soils and particle-size fractions represent various horizons from four freely drained and three poorly drained profiles covering four main soil associations in north-east Scotland. The profile characteristics, including the distribution of organic and inorganic phosphorus, have already been described (Williams and Saunders, 1956) together with the procedure for large-scale separation of the particle-size fractions. The depths of sampling and the nature of the parent till are given in Table 6.

The essential features of the extraction methods are as follows:

Acetic-acid method (*Williams and Stewart, 1943*): 2-hour extraction with 2·5 per cent. by vol., acetic acid, with extractant:solid ratio of 40:1.

Truog method (*Truog, 1930*): 30-min. extraction with 0·002 N H_2SO_4, buffered with ammonium sulphate to pH 3, with extractant:solid ratio of 200:1.

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Lactate method (*Egnér, 1932*): 2-hour extraction with 0·02 N calcium lactate in 0·01 N HCl, pH 3·8, with extractant:solid ratio of 50:1.

Phosphate-sorption capacity: Saturation with phosphate at pH 4 followed by NaOH extraction according to the method of Piper (1947) for anion-exchange capacity.

Inorganic phosphorus was determined colorimetrically in the extracts using the stannous-chloride method as described by Williams and Stewart (1941).

Results for Particle-size Fractions

Standard extractions (*Tables 1 and 2*). At the conventional 40:1 ratio the acetic extraction (Table 1) attacks the fine sands to very marked extents. In most of the samples the acetic value is highest for this fraction and the proportion of the total inorganic phosphorus extracted is of the order of 20–40 per cent. The acetic method also extracts consider-

TABLE 1

Acetic Extractions of Particle-size Fractions at 2 hrs.

	mg. P_2O_5 *per 100 g. fraction*†								*% extraction of total inorganic P at standard ratio*			
	Standard, 40:1, ratio				*'Soil ratios'*‡							
*Sample no.**	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	*Coarse sand*	*Fine sand*	*Silt*	*Clay*
1*a*	9·9	23·6	10·0	6·9	6·2	27·9	17·8	26·2	8	23	9	2
1*b*	3·1	19·3	5·9	2·3	4·3	20·1	9·9	5·6	4	25	8	1
2*a*	18·8	25·4	13·7	7·0	21·6	31·0	21·8	27·6	11	26	15	3
2*b*	1·1	13·3	3·0	1·5	2·5	14·6	4·7	4·4	5	19	4	1
3*a*	4·6	39·6	3·5	1·8	6·3	62·4	16·3	4·7	4	18	2	0
3*c*	2·4	33·8	2·3	0·9	3·1	45·3	6·9	2·1	2	18	1	0
3*d*	1·9	20·6	2·8	0·9	2·1	29·2	10·2	3·1	2	14	2	0
4*a*	6·8	73·0	14·5	8·7	7·7	104	63·5	35·8	6	22	6	2
4*b*	5·7	79·6	32·4	0·4	6·5	122	99·5	0·7	7	23	18	0
4*c*	4·6	71·5	21·7	0·4	5·0	98·2	81·5	0·8	6	23	11	0
5*a*	7·1	16·6	4·1	7·9	3·0	26·8	19·3	62·1	25	23	3	2
5*b*	2·0	18·0	1·6	2·4	1·9	24·8	8·6	9·4	6	17	1	1
5*c*	4·9	104	66·4	5·8	3·5	104	144	41·1	9	34	32	2
6*a*	4·5	31·4	3·2	9·4	7·3	44·5	27·0	62·5	9	22	3	2
6*b*	7·9	72·8	25·6	0·5	6·8	75·5	27·9	1·9	18	42	44	1
6*c*	16·6	100	66·9	0·5	13·1	102	92·0	1·7	21	43	67	1
7*a*	10·0	52·7	5·7	5·6	1·4	58·2	10·9	29·3	5	35	4	1
7*b*	1·1	0·6	0·7	1·0	0·7	0·7	0·9	2·3	1	1	0	0
Means	6·3	44·2	15·8	3·5	5·8	55·1	37·8	17·9	8	24	13	1

* For profile identifications see Table 6.

† All P values in all tables are expressed on the oven-dry basis.

‡ 'Soil ratio' $= \frac{\text{Standard ratio} \times 100}{\%\text{ fraction in soil}}$.

able amounts of phosphorus from the coarse sands, but in keeping with the larger particle size the proportions extracted are much lower. The Truog extraction (Table 2) also dissolves considerable amounts of phosphorus from the sands, but as shown by the mean proportions extracted it is about one-third as effective as the acetic method. The lactate extraction has practically no effect on the coarse sands, and little effect on the fine sands.

The silt fractions, particularly from the topsoils, contain appreciable amounts of clay (Williams and Saunders, 1956) and the significance of

TABLE 2

Standard Truog and Lactate Extractions of Particle-size Fractions

Sample no.	mg. P_2O_5 per 100 g. fraction: Truog: Coarse sand	Truog: Fine sand	Truog: Silt	Truog: Clay	Lactate: Coarse sand	Lactate: Fine sand	Lactate: Silt	Lactate: Clay	% extraction of total inorganic P by Truog method: Coarse sand	Fine sand	Silt	Clay
1a	3·1	11·1	13·2	34·8	Trace	2·8	2·0	9·1	3	10	12	8
1b	1·2	5·8	11·3	10·7	Trace	0·5	0·4	2·2	2	8	15	5
2a	5·8	7·3	15·4	31·4	Trace	3·5	2·7	11·0	4	7	17	14
2b	1·2	4·4	6·2	6·9	Trace	0·5	0·6	1·7	1	6	9	4
3a	1·9	12·1	9·2	5·1	0·6	0·9	0·6	0·7	2	5	4	1
3c	0·8	9·3	4·3	1·1	Trace	0·3	0·2	0·2	1	5	2	0
3d	0·8	6·6	4·4	1·5	Trace	0·3	0·3	0·2	1	5	3	1
4a	3·1	15·9	15·5	37·6	0·9	1·9	2·2	5·8	3	5	7	10
4b	1·8	26·6	39·2	1·0	0·2	0·3	0·1	0·1	3	8	20	1
4c	2·0	20·8	21·8	0·8	Trace	0·4	0·1	0·1	3	7	11	1
5a	5·2	8·4	10·5	12·0	1·4	3·4	2·1	3·6	19	12	8	3
5b	1·0	3·9	3·0	0·7	Trace	0·4	0·4	0·7	3	4	2	0
5c	1·4	14·3	31·6	8·1	Trace	0·4	0·1	1·8	3	5	15	3
6a	1·8	8·4	7·8	27·7	Trace	1·8	2·2	7·1	4	6	7	7
6b	1·4	16·2	17·9	2·5	0·1	0·4	0·1	0·1	3	9	31	4
6c	2·4	21·4	40·8	2·5	0·1	0·4	0·2	0·2	3	9	39	5
7a	4·2	18·7	13·9	2·2	Trace	1·7	2·1	4·5	2	13	10	4
7b	0·5	1·4	1·9	1·3	Trace	0·3	0·1	0·1	0	2	1	0
Means	2·2	11·8	14·9	11·6	0	1·1	0·9	2·7	3	7	12	4

the results is therefore uncertain. It is clear, however, that the Truog and acetic methods are capable of extracting considerable amounts, indicating the presence of calcium-bound phosphorus. The lactate method again has relatively little effect.

The outstanding feature of the clay results is the relatively high effectiveness of the Truog extraction. The mean values show it to be about three times more effective than the other two methods, which give very similar results. Even for the Truog method, however, the proportions of the clay inorganic phosphorus extracted are low.

The changes in the values with depth are very similar, and in keeping with the total inorganic-phosphorus contents of the fractions (Williams and Saunders, 1956).

Effect of acetic acid:fraction ratio (*Tables 1 and 3*). When a soil is extracted by the standard method the proportion of total acetic acid

TABLE 3

Effect of Extractant: Solid Ratio and Period of Extraction on Acetic Values for Fine Sands and Clays—mg. P_2O_5 per 100 g. Fraction

Sample no.	Effect of ratio at 2 hrs.: Fine sands 40:1	Fine sands 200:1	Clays 40:1	Clays 200:1	Effect of time at 'soil ratios'*: Fine sands 5 min.	Fine sands 30 min.	Fine sands 2 hrs.	Fine sands 48 hrs.	Clays 5 min.	Clays 30 min.	Clays 2 hrs.	Clays 48 hrs.
1a	23·6	27·2	6·9	30·0	6·6	14·1	27·9	45·6	26·4	27·7	26·2	30·8
2a	25·4	28·0	7·0	28·0	6·6	14·6	31·0	45·1	30·4	29·7	27·6	18·9
3a	39·6	66·4	1·8	5·0	3·0	17·0	62·4	134	5·1	4·5	4·7	6·9
4a	73·0	109	8·7	32·6	5·8	26·9	104	220	36·3	39·0	35·8	20·3
5a	16·6	18·7	7·9	35·8	..	..	..	..	..	..	..	..
6a	31·4	36·8	9·4	42·4	..	..	..	..	..	..	..	..
7a	52·7	65·4	5·6	30·4	4·5	21·8	58·2	76·8	26·0	29·1	29·3	22·1

* See footnote, Table 1.

to each individual fraction is greater than 40:1 and depends on the particle-size composition. This wider ratio will be called the 'soil ratio' for the fraction. In connexion with the '*F*-values', which are discussed later, each fraction has been extracted with acetic acid at its 'soil ratio'. In practice, the weight of air-dry fraction present in 2 g. air-dry soil was extracted with 80 ml. acetic acid. The results are given in Table 1.

All the 'soil ratios' are much higher than 40:1, but, since they vary considerably depending on the particle-size composition of the soils, strict comparisons of the two sets of values in Table 1 are possible only for each individual fraction. The effect of increasing the ratio for the coarse sand is on the whole small and rather inconsistent, but all the fine-sand and silt values are clearly higher at the wider 'soil ratios'. Several of the increases shown by the latter two fractions are considerable, but they are all much smaller than for the clays, which show increases of up to sevenfold. The much greater effect of acetic:fraction ratio for the clays is confirmed by the direct comparisons in Table 3 between extractions at 40:1 and 200:1 on the clays and fine sands from the topsoils.

Effect of period of extraction with acetic acid (*Table 3*). To obtain the maximum effect that can occur during the normal extraction of the soil, the fine sands and clays from five of the topsoils were extracted for periods ranging from 5 min. to 48 hrs., using the 'soil ratios'. The results show a marked contrast in behaviour between the fine sands and clays. For the sands the phosphorus in solution increases exponentially with time, and the curves when plotted show that there is little change after about 10 hrs. Except for sample 3*a*, the values for the clays reach a maximum at a short period and then decrease with time. It is clear that the clay extractions involve side reactions and are inherently different from the sand extractions.

Discussion. The results for the sand fractions are readily understood on the basis that the dominant process is a dissolution of acid-soluble, mainly calcium-bound, phosphorus (Williams and Saunders, 1956) from relatively coarse particles, the effectiveness of the extraction depending mainly on the particle size, pH, and period of contact. The low effectiveness of the lactate extraction probably depends on the common-ion effect of the calcium present, but can be attributed mainly to its relatively high pH of 3·8, compared with 2·6 for the acetic extraction and 3·0 for the Truog. The results in Table 3 indicate that the dominant factor in the superiority of the acetic extraction over the Truog method is the longer period of extraction. This advantage and the somewhat lower pH of the acetic method are counteracted by the much wider extractant:solid ratio in the Truog extraction, but Table 3 shows that for the sands this factor is much less important than the period of extraction. The exponential variation with time is most simply understood on the basis that the rate of solution is proportional to the amount of phosphorus still undissolved. The rate of solution can also be related to the difference in phosphate concentration between the bulk extract and the concentrated films of liquid at the particle surfaces (Moelwyn-Hughes, 1947). The lower the concentration in the bulk extract the higher this difference, and the higher the rate of diffusion and solution of phosphate. On this basis

the appreciable increases in the acetic values produced by widening the acetic:fine-sand ratio (Table 3) can be interpreted as increases in the rate of solution, arising from the lower concentrations of phosphate in the more dilute suspensions.

The clay extractions involve more than one reaction, but the dominant process in the initial stage is desorption of the adsorbed, readily exchangeable, surface phosphate, tending towards an equilibrium distribution between the surfaces and the solution. This accounts for the extreme rapidity of extraction and the large increases with increasing extractant: clay ratio (Table 3). The marked superiority of the Truog method on the clays is undoubtedly attributable mainly to its much wider ratio resulting in lower concentrations of phosphate in solution and thereby increasing the desorption of the surface phosphate. A wide extractant: clay ratio also militates against removal of phosphate from solution by secondary reactions; in particular, lower concentrations of phosphate and cations, especially iron, make the conditions less favourable for precipitation. The acetic and lactate methods have the same extraction period, and since the acetic 'soil ratio' values in Table 3 show very little change between 30 min. and 2 hrs. it can be taken that this difference does not materially affect the comparisons with the standard Truog values. The Truog reagent, however, is 0·02 N with respect to sulphate and at the pH prevailing the divalent sulphate ions enhance the extraction of phosphorus (Williams and Stewart, 1943; Mattson *et al.*, 1950). The monovalent acetate anions are less effective, but at the concentration and pH obtaining they probably enhance the extraction to some extent. The anion effect can be expected to be more important in the lactate method. By virtue of their hydroxyl and carboxyl groups the lactate ions release phosphate by forming complexes with iron and aluminium (Swenson *et al.*, 1949). This factor counteracts, and may well largely counterbalance, any disadvantage arising from the higher pH of the lactate extraction. From these considerations it is unlikely that the relationships between the clay values by the three standard methods are greatly affected by the differences in period of extraction, pH, and the nature of the anions, and there is no doubt that the dominant factor is the extractant:clay ratio.

Calculation and significance of F-*values.* The term '*F*-value' (Williams and Saunders, 1956) is used for convenience to denote the amount of constituent in a particle-size fraction in 100 g. soil. For example, if the soil contains y per cent. of clay containing f mg. P_2O_5 per 100 g., then the *F*-value for the clay (per 100 g. soil) = $yf/100$ mg. P_2O_5.

Apart from analytical errors there is no difficulty in determining *F*-values for total phosphorus. The sum of the *F*-values agrees with the value for the original soil, and they provide valid estimates of the contributions of the particle-size fractions to the soil values. This is true also for phosphorus extracted by strong agents, such as 0·2 N H_2SO_4, that extract large amounts and are little affected by changes in the extraction conditions. With mild extractants like those used in the acetic, Truog, and lactate methods the position is more complicated. In addition to inherently higher analytical errors the fact that the values, especially for the clays, depend on the extractant:solid ratio has to be considered. All

three reagents are strongly buffered and at the ratios concerned there is no appreciable consumption of the reagent during the extraction. During soil extractions, therefore, it is appropriate to regard each particle-size fraction as being subject to attack by all the extractant added. From this point of view, *F*-values calculated from extractions on the individual fractions at the standard extractant:solid ratios are too low; they represent the minimum potential contributions of the fractions to the soil values. The alternative is to adjust the ratio for each fraction according to the particle-size composition of the soil to give the so-called 'soil ratios' already mentioned. The 'soil ratio' *F*-values represent the maximum possible contributions of the fractions to the soil values, and are undoubtedly more appropriate, particularly for the clays. The validity of the *F*-values in relation to the original soil values is also subject to uncertainties arising from losses of readily soluble phosphorus and modifications of the fractions, particularly their surface properties, during the prolonged treatments involved in the separations. The influence of such factors, however, can be assessed by extracting the reconstituted soils, prepared by mixing the fractions in the proportions in which they were obtained.

Acetic F-*values* (*Table 4*). To save space individual *F*-values are given

TABLE 4

Contributions of Fractions to Acetic Soil Values

Sample no.	'Soil ratio' F-values*				mg. P_2O_5 per 100 g. soil			Ratios		% contributions‡ of fractions to reconstituted soil values			
					Sums of F-values		Reconstituted† soil at standard ratio C						
	Coarse sand	Fine sand	Silt	Clay	'Soil ratios' A	Standard ratio B		A/C	B/C	Coarse sand	Fine sand	Silt	Clay
1a	1·2	9·8	4·5	6·0	21·5	14·0	11·0	2·0	1·3	3	29	13	55
1b	0·9	6·6	2·2	1·5	11·2	8·9	3·5	3·2	2·5	5	39	13	43
2a	3·9	12·1	5·0	6·0	27·0	17·9	11·9	2·3	1·5	9	29	12	50
2b	0·4	5·1	1·2	1·1	7·8	6·1	2·9	2·5	2·1	4	47	11	38
3a	1·7	21·2	8·4	0·9	32·2	15·7	3·9	8·2	4·0	4	52	21	23
3c	1·0	15·9	1·3	0·3	18·5	13·1	3·3	5·6	4·0	5	79	7	9
3d	0·7	10·5	1·5	0·5	13·2	8·5	2·7	5·0	3·1	5	67	9	19
4a	2·3	38·4	10·8	5·8	57·3	32·8	17·8	3·2	1·9	3	50	14	33
4b	2·3	47·6	12·9	0·1	62·9	37·3	9·0	7·0	4·2	4	75	20	1
4c	0·1	42·2	11·4	0·1	53·8	35·3	4·3	12·5	8·2	0	77	21	2
5a	1·5	7·2	2·5	6·2	17·4	9·3	8·2	2·2	1·1	3	16	5	76
5b	0·9	7·2	1·3	0·7	10·1	6·6	2·2	4·6	3·0	7	52	9	32
5c	1·7	31·2	20·2	2·9	56·0	43·3	31·5	1·8	1·4	4	53	34	9
6a	1·5	7·2	2·5	6·2	17·4	10·7	9·2	1·9	1·2	4	21	8	67
6b	2·8	26·4	4·7	0·2	34·1	33·2	26·2	1·3	1·3	9	77	13	1
6c	6·7	26·6	10·1	0·2	43·6	42·0	29·9	1·5	1·4	15	61	23	1
7a	0·3	16·3	3·4	7·0	27·0	10·7	8·9	3·0	2·2	0	17	4	79
7b	0·1	0·4	0·2	0·2	0·9	0·8	0·2	4·2	4·0	..	..	..	..

* *F*-value = mg. acetic soluble P_2O_5 per amount of fraction in 100 g. soil.
† Compare with values for original soils in Table 6.
‡ See text for basis of calculation.

only for the extractions at the 'soil ratios'. The main feature of the results is that the sums of *F*-values for both ratios are much higher than the values for the reconstituted soils. Since the sums of the standard *F*-values, representing the minimum contributions of the fractions, are clearly higher than the values for the reconstituted soils, there is no doubt

that there are marked negative interactions between the fractions. As already indicated, however, the amount of interaction is more adequately reflected by the sums of the 'soil ratio' *F*-values. For most of the samples the acetic value for the reconstituted soil (Table 4) is markedly lower than for the original soil (Table 6). This can be attributed to some extent to losses of readily soluble phosphorus during the separation of the fractions, but almost certainly the main cause is activation of the clays during the separations, resulting in greater interaction between the fractions in the reconstituted soils.

Apart from the marked interactions between fractions, the acetic *F*-values do not therefore provide a simple reliable basis for calculating the relative contributions of the fractions to the normal soil values. However, it is clear that the coarser fractions have a substantial influence and estimates of their relative contributions to the values for the reconstituted soils are given in Table 4. These estimates are based on the assumptions that the total contribution of the three coarser fractions is given by the difference between the value for the reconstituted soil and the 'soil ratio' *F*-value for the clay, and that their relative contributions are in the same proportions as their 'soil ratio' *F*-values. Since the 'soil ratio' *F*-value represents the maximum potential contribution of the clay, the values for the coarser fractions are minimum contributions. The apparent total contribution of the three coarser fractions to the acetic values for the topsoils is of the order of 20–80 per cent., the dominant fraction being the fine sand with 16–52 per cent., compared with 4–21 per cent. for the silt and 0–9 per cent. for the coarse sand. In the subsoils the total influence of the coarser fractions is even higher and in several cases they apparently account for over 90 per cent. of the acetic value. In all cases the major portion is again contributed by the fine sand and it is noteworthy that the general level of the values for this fraction is highest in the basic igneous profiles, 3 and 4. These features are in accord with the contributions of the fine sand to the total soil inorganic phosphorus (Williams and Saunders, 1956).

Truog F-*values* (*Table* 5). The sums of the standard Truog *F*-values are in many cases very similar to the values for the reconstituted soils, but unlike the acetic results the general tendency, especially for the topsoils, is for the reconstituted soil value to be the higher. As already explained, this tendency is due to the *F*-values based on the standard ratio being too low, and does not mean that there are positive interactions between the fractions, but the fact that the sums of the standard Truog *F*-values, particularly in the topsoils, are smaller than the values for the reconstituted soils indicates that any interaction is probably small, and certainly much less than in the acetic method. In agreement with these conclusions, the Truog values for the original and reconstituted soils (Tables 6 and 5), are in most cases similar and in better agreement than the corresponding acetic values (Table 4). Unlike the acetic results, the differences in the Truog values show no consistent trend and are probably due in most cases to experimental variations.

The lower interaction between fractions and the general similarity between the original and reconstituted soil values strengthen the validity

TABLE 5

*Contributions of Fractions to Truog Soil Values**

Sample no.	Standard ratio F-values				mg. P_2O_5 per 100 g. soil		Ratio	% contributions of fractions to reconstituted soil values			
	Coarse sand	Fine sand	Silt	Clay	Sum of F-values A	Reconstituted soil B	A/B	Coarse sand	Fine sand	Silt	Clay
1a	0·6	3·9	3·3	7·3	15·1	18·8	0·8	3	21	17	59
1b	0·2	1·9	2·5	2·8	7·4	7·8	0·9	3	26	34	37
2a	1·0	2·8	3·5	6·3	13·6	19·6	0·7	5	14	18	63
2b	0·2	1·5	1·5	1·8	5·0	5·4	0·9	4	30	30	36
3a	0·5	4·1	1·9	0·9	7·4	10·1	0·7	5	40	19	36
3c	0·3	3·2	0·8	0·2	4·5	4·2	1·0	7	70	18	5
3d	0·3	2·4	0·7	0·2	3·6	4·3	0·8	9	66	19	6
4a	0·9	5·9	2·6	5·7	15·1	21·1	0·7	4	28	12	56
4b	0·6	10·4	5·1	0·1	16·2	19·1	0·8	4	63	32	1
4c	0·5	9·0	3·1	0·1	12·7	10·2	1·2	4	70	25	1
5a	2·6	2·3	1·4	1·2	7·5	16·6	0·5	15	14	8	63
5b	0·5	1·5	0·5	0·1	2·6	2·8	0·9	19	58	19	4
5c	0·7	3·9	4·4	0·6	9·6	12·4	0·8	7	40	47	6
6a	1·0	1·8	1·0	3·1	6·9	13·0	0·5	8	14	8	70
6b	0·6	5·7	3·0	0·2	9·5	9·6	1·0	6	60	32	2
6c	1·2	5·6	4·5	0·3	11·6	11·0	1·0	10	49	38	3
7a	0·8	5·2	4·3	4·9	15·2	26·2	0·6	4	24	17	55
7b	0·1	0·7	0·5	0·1	1·4	2·9	0·5	7	50	36	7

* See footnotes, Table 4.

of the Truog *F*-values as estimates of the contributions of the fractions to the soil values, but the fact that they are based on the standard ratio has to be taken into account. Since the effect of extractant:fraction ratio is relatively small for the coarser fractions (Table 3) and the standard Truog ratio is already very wide, there can be no serious discrepancy in using the standard instead of the 'soil ratio' *F*-values for these fractions. The 'soil ratio' *F*-values for the clays, however, may be appreciably higher than the standard values, particularly where the clay is rich in phosphorus. This doubtless accounts for the fact that in all the topsoils the reconstituted soil value is higher than the sum of the standard *F*-values. In such cases it is reasonable to accept that a much fairer estimate of the clay contribution is obtained by increasing the standard *F*-value by the amount of the difference between the reconstituted soil value and the sum of the standard *F*-values. On this basis the relative contributions of the fractions to the soil values are obtained by expressing the adjusted *F*-value for the clay and the standard *F*-values for the other three fractions as percentages of the value for the reconstituted soil. The results for the topsoils in Table 5 have been calculated in this way, but for the subsoils, where the clay is less important and the reconstituted soil values are very similar to the sums of *F*-values, the simpler method of expressing the standard *F*-values as percentages of the sum of *F*-values has been used. The three coarser fractions account for 30–60 per cent. of the Truog values for the topsoils and in most instances more than 90 per cent. of the values for the subsoils. The contributions of the coarse sand are mostly of the order of 5 per cent., compared with 14–70 per cent. for the fine sands and 8–47 per cent. for the silts. The main contrast with the acetic results in Table 4 is that the Truog values are less affected by

the fine sands but more affected by the silts. The influence of the fine sands is again highest in the basic igneous soils.

Lactate method. The inherently higher errors and the limited data available preclude reliable calculations of the composition of the lactate values. From Table 2 the indications are that the topsoil values reflect mainly the adsorbed phosphorus of the clay, but in the subsoils, where the clay values are low, the coarser fractions have considerable influence.

Interactions between fractions. Since the reconstituted soils were prepared by mixing the air-dry fractions shortly before adding the extractant, physical factors such as protective coating of the sands by the clay can be discounted. It follows, therefore, that the interactions between fractions in the reconstituted soils are largely chemical. Comparisons of the acetic results for different soils show that high interaction is associated with high acid-soluble phosphorus in the coarser fractions, particularly the fine sands, and high phosphate-sorption capacity of the soil. This indicates that the dominant process is sorption by the clay of phosphorus derived from the sands and silt. The occurrence of such reactions during dilute acid extractions of soils is well known (Russell and Prescott, 1916; Williams, 1950).

The relative amounts of interaction in the different soils are conveniently represented by the ratios of the sums of *F*-values to the values for the reconstituted soils (Table 4). The influence of the fine sand is illustrated by the basic igneous soils, profiles 3 and 4, where the fine sands are rich in acetic-soluble phosphorus (Table 1) and account for 35–70 per cent. of the total soil inorganic phosphorus (Williams and Saunders, 1956). In keeping with this the interaction is high throughout both profiles, and is highest in the poorly drained subsoils which also have the highest acetic values for the fine sands (Table 1). The relationship also depends on the phosphate-sorption capacity of the clay. Other things being equal, the degree of resorption of sand phosphorus should be higher the higher the phosphate-sorption capacity of the clay, and some indications of this effect are suggested by the sorption capacities of the soils (Table 6). For example, the sorption capacity is very high for samples 3*a*, 3*b*, 3*c*, and 7*b*, and so also is the interaction between fractions (Table 4). Conversely, the low sorption capacity of the granitic subsoils 5*c*, 6*b*, and 6*c*, is in keeping with the fact that the interactions during the acetic extractions are relatively low, considering the high acetic values for the sands (Table 1).

The above interpretation also explains the much lower interaction during the Truog extraction (Table 5), compared with the standard acetic extractions (Table 4). Not only does the much wider Truog ratio make the conditions less favourable for sorption of phosphate by clay, but the shorter period also results in much lower extraction of phosphorus from the sands. In the latter connexion, it is particularly noteworthy that the fine-sand phosphorus from the basic igneous soils is much less soluble in the Truog extraction (Table 2) than in the acetic extraction (Table 1). In agreement with this the Truog results for the basic igneous soils (Table 5) are very similar to those for the other soils, whereas the acetic interactions (Table 4) are higher.

TABLE 6

Values for Original Soils

Sample no.	Depth (inches)	Sorption capacity ($\%P_2O_5$)	mg. P_2O_5 per 100 g. soil		
			Acetic	Truog	Lactate
Freely drained profile on Old Red Sandstone till—Laurencekirk Association					
1*a*	0–6	1·32	19·6	23·2	8·2
1*b*	10–14	1·39	5·5	6·6	1·3
1*c*	17–21	1·35	6·2	6·4	2·2
Poorly drained profile on Old Red Sandstone till—Laurencekirk Association					
2*a*	0–6	0·58	27·8	29·8	12·7
2*b*	9–13	0·94	5·1	5·8	1·5
2*c*	15–19	0·81	4·1	4·1	0·9
Freely drained profile on basic igneous till—Insch Association					
3*a*	0–6	2·60	6·8	9·6	0·9
3*b*	8–13	2·66	2·8	4·4	0·2
3*c*	15–17	2·48	3·2	4·1	0·3
3*d*	18–21	1·79	3·5	4·4	0·4
3*e*	26–30	1·13	2·0	4·9	0·4
Poorly drained profile on basic igneous till—Insch Association					
4*a*	0–6	1·32	26·6	16·7	5·0
4*b*	10–14	1·08	18·7	15·3	0·1
4*c*	18–22	1·22	11·3	12·4	0·2
4*d*	26–30	1·15	5·4	8·4	0·2
4*e*	36–42	1·39	5·3	6·9	0·1
Freely drained profile on granitic till—Countesswells Association					
5*a*	0–8	1·08	12·1	13·9	5·1
5*b*	10–14	1·69	3·3	3·5	0·7
5*c*	14–20	0·56	38·0	12·8	1·9
5*d*	27–30	0·32	61·1	22·6	2·3
Poorly drained profile on granitic till—Countesswells Association					
6*a*	0–8	0·81	12·9	12·7	5·8
6*b*	11–16	0·22	31·7	12·0	0·2
6*c*	22–27	0·28	34·7	13·5	0·1
6*d*	33–39	0·19	52·5	17·9	0·1
Freely drained profile on slate till—Foudland Association					
7*a*	0–8	1·51	24·6	24·2	6·9
7*b*	12–18	2·50	0·5	2·1	0·3
7*c*	24–30	1·03	1·9	3·1	0·3
7*d*	36–40	0·97	1·2	2·2	0·3

Results for Soil Extractions (Table 6)

The results for the fractions taken in conjunction with the factors noted above provide a rational explanation of the absolute and relative behaviour of the three methods on the different soils. The lower magnitude of, and variations in, the lactate values are readily understood on the

basis that they reflect mainly the adsorbed phosphorus of the clay. In general, the lactate value is higher the higher the phosphorus content of the clay and the lower the phosphate-sorption capacity of the soil. Thus the much higher lactate values of the topsoils compared with the subsoils reflect the much higher inorganic phosphorus of the clays in the former (Williams and Saunders, 1956). The bulk of the inorganic phosphorus in the subsoils is present in the sand fractions, and as noted earlier the lactate extraction attacks the coarser fractions to only very small extents (Table 2). The effect of sorption capacity is best shown by comparing the corresponding freely drained and poorly drained soils. The freely drained soils have higher contents and proportions of inorganic phosphorus in the clays (Williams and Saunders, 1956), but the lactate values for the topsoils are lower than for the poorly drained soils. The reason is that the lower sorption capacity in the poorly drained soils results in greater desorption of the clay.

Like the lactate values, the acetic and Truog values tend to vary inversely with the sorption capacity of the soil, but in keeping with the more effective desorption of the clay the Truog values are less affected than the acetic. Unlike the lactate extraction, however, the acetic and Truog extractions, especially the former, reflect the phosphorus in the sands, particularly the fine sand. As a result, the values tend to be higher the higher the phosphorus contents of the sands, the effect being greater the lower the sorption capacity of the soil. The following examples illustrate these points.

The effect of high sand phosphorus (Table 4) coupled with low phosphate-sorption capacity is shown by the granitic subsoils 5*c*, 5*d*, 6*b*–6*d*. This combination results in abnormally high acetic values because, as illustrated by the lower interactions in Table 4, there is relatively little sorption by the clay and high proportions of the phosphorus dissolved from the sands remain in solution. For the same reason, the much greater effectiveness of the acetic extraction compared with the Truog method on the sands appears as much higher acetic values for the soils. Similarly, the general trend for the acetic values to increase down the granitic profiles is explained by parallel increases in the acetic values for the sands (Table 4) reinforced by decreases in the phosphate-sorption capacity (Table 6). The Truog values in these profiles vary in a similar manner, but because of the lower effectiveness on the sands and the lower sensitivity to sorption capacity, the changes are smaller. The only irregularity in the increases in the acetic values is that the first subsoil, 5*b*, has the lowest value in the freely drained profile, but it has also the lowest acetic values for the sands and silt and a higher sorption capacity. Higher sand phosphorus coupled with lower sorption capacity also contributes to the higher acetic values in the poorly drained compared with the freely drained topsoils, and again the contrast is less pronounced for the Truog method.

The effect of very high sorption capacity is illustrated by the freely drained basic igneous soils 3*a*–3*c* (Table 6). In these soils the strong sorption is the dominant factor and despite high values for the sands (Table 4) the acetic values for the soils are low. The Truog values are

also low, but because of the more effective desorption of the clay they are higher than the acetic values.

General Discussion

The results demonstrate the importance of extractant:solid ratio, period of extraction, and pH as experimental factors, and of phosphate-sorption capacity and distribution of phosphorus over the particle-size fractions as soil properties. The relative and absolute behaviour of the three methods on the soils and fractions is explained by the varying balance of these factors.

The estimated contributions of the fractions to the acetic and Truog soil values involve uncertainties. Even so, it is clear that in most instances the subsoil values are derived mainly from the acid-soluble phosphorus in the coarser fractions, particularly the fine sands. There is also strong evidence that the fine sands and silts make major contributions to the topsoil values, and that their influence depends on the parent material, being highest in the basic igneous soils. In considering the possible implications of this in relation to the usefulness of the values as criteria of phosphate status several factors have to be taken into account. In these acid soils the phosphorus in the coarser fractions is potentially available. The object of the extraction methods is to obtain an integrated expression of phosphate status, and some reflection of the sand and silt phosphorus in the soil values may therefore be appropriate; but pronounced influence is not desirable because there is no evidence that the short-term contribution to crops is important and the particle size, particularly for the sands, militates against this possibility. Caution is therefore necessary in using acetic and Truog values as a guide to the potential contribution of subsoils to the phosphate nutrition of crops, particularly where the sorption capacity is low and the values are high due to relatively unrestricted extraction of sand phosphorus.

For the topsoils a limited comparison can be made between the present data and crop-response correlations for the different soil groups (Williams, Reith, and Inkson, 1952). The results suggest that poor acetic correlations, particularly for the basic igneous soils, may be due to some extent to high influence of the coarser fractions on the extraction values, but there is no consistent relationship to justify the conclusion that this is a major factor governing the usefulness of the three methods. Since topsoils have high sorption capacities there is the overriding consideration that both the uptake of phosphorus by plants and its concentration in the soil extracts are ultimately controlled by the clay.

In conclusion, attention is drawn again to the extreme behaviour of the freely drained basic igneous soils which are characterized by high sand phosphorus and high sorption capacity. This combination results in exceptionally high interaction between fractions during the acetic extraction, which in turn supports the earlier finding (Williams, 1951) that acetic-acid treatment of these soils produces extensive redistribution of phosphorus. It was also found that following the acid treatment there is a marked increase in phosphorus extracted by neutral ammonium fluoride. This result provides strong confirmation of the view that the

interaction between fractions involves mainly the conversion of calcium-bound phosphorus from the coarser fractions into sesquioxide-bound phosphorus of the clay, because neutral ammonium fluoride has little effect on the former, but is highly effective on the latter.

Summary

1. Particle-size fractions from samples representing seven soil profiles have been extracted individually and in combination by the acetic, Truog, and lactate methods to assess their significance in soil extractions.

2. Extraction of phosphorus from the sands is very marked by the acetic method, considerable by the Truog, and very low by the lactate. The dominant process appears to be dissolution of calcium-bound phosphorus from coarse particles, because the values are higher the lower the pH and particle size, increase exponentially with time, but are not greatly affected by extractant:solid ratio.

3. The Truog method is much the most effective on the clays and the acetic values are somewhat higher than the lactate. The dominant factor is the much wider extractant:solid ratio in the Truog method because the extraction of the clay is primarily a desorption of the adsorbed phosphorus. The values increase markedly with extractant:solid ratio, reach a maximum in a short time, and fall during longer periods due to removal of phosphate from solution by secondary reactions.

4. Acetic extractions of reconstituted soils, prepared by mixing the appropriate amounts of fractions, give much lower values than are obtained by calculation from extractions on the individual fractions, showing that there are negative interactions between them. The main factor appears to be sorption by the clay of phosphorus dissolved from the sands. The interaction is higher the higher the phosphorus in the sands and the higher the phosphate-sorption capacity of the soil, and is greatest for the basic igneous soils, where both these values are high.

5. The corresponding results for the Truog method indicate relatively little interaction between fractions, the main reasons being that the shorter extraction dissolves less phosphorus from the sands while the wide extractant:solid ratio is unfavourable for sorption by the clay.

6. The values for the original soils are in keeping with the above conclusions. The phosphorus in solution in all three extracts is controlled by the clay, and the values vary inversely with the phosphate-sorption capacity of the soil. Where the sorption capacity is high, all the values are low, but because of the wide ratio the Truog values are higher than the others. Where the sorption capacity is low and the sands are rich in phosphorus, both the acetic and Truog values are high, but the former are much higher than the latter because of the much higher effectiveness of the acetic extraction on the sands.

7. The lactate values reflect mainly the adsorbed phosphorus of the clay, but the acetic and Truog values are markedly influenced by the coarse fractions and in most of the subsoils appear to be derived mainly from these sources, particularly the fine sand. The implications of this in relation to the evaluation of phosphorus status are discussed.

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EXCHANGEABLE CATIONS IN SOLODIZED-SOLONETZ AND SOLONETZ-LIKE SOILS OF SASKATCHEWAN*

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Introduction

SOLONETZIC soils present many problems in soil classification, nomenclature, and mapping. The term 'solonetzic' is here used to describe the complex group of soils associated with saline parent materials, and characterized by a predominance of profiles having platy-structured A horizons and columnar-structured B horizons. The latter are more compact and heavier in texture than the A horizons. The various profiles of the solonetzic group are distinguished by differences in morphological features which can be related to differences in conditions of salinity, alkalinity, and acidity. Thus the solonetzic soils range from the saline and alkaline solonetz to the non-saline, acidic solod.

Solonetzic soils, as defined above, are widely distributed in Saskatchewan, occurring in all the major soil zones. Current studies of these soils will, it is hoped, assist in arriving at a more satisfactory definition and classification of the various profiles. Such information is required for the more detailed soil surveys now in progress, and as an aid to the development of an acceptable world classification of soils. It is also hoped that the study will contribute to an understanding of the genesis of solonetzic soils.

The present paper represents a portion of the main study, and is concerned with the exchangeable cations found in the solodized-solonetz soils and in other soils characterized by less-strongly developed solonetzic profiles, tentatively referred to as solonetz-like soils. Determinations of pH and conductivity are also reported. Additional information on total nitrogen, organic and inorganic carbon, and mechanical analysis are not given in the present paper.

Description of Soils

Generalized descriptions of the two groups of genetic profiles used in this study are given below. The number of profiles is too large to permit the presentation of individual profile descriptions. In addition, the profiles belonging to a given genetic group are essentially similar in morphology, and hence can be covered by a general description. A separate discussion is given of the podzolic-solonetzic profile. In the following descriptions, horizon B_1 refers to the upper portion of the true B horizon, and therefore corresponds to the American B_2 horizon; cloddy structures consist of medium to large cubic aggregates with rough or irregular sides.

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Generalized Description of Solodized-Solonetz Profiles

A_1 horizon	The colour usually reflects the A_1 colours of the zone in which the profile occurs; cloddy to cloddy-platy structures; 4 to 5 in. thick.
A_2 horizon	Light coloured (pale brown to grey); cloddy-platy or thick platy structures; 3 to 4 in. thick.
A_3 horizon	Grey to light grey; thin platy; may be absent; usually 0 to 2 in. thick; sometimes 3 to 4 in. thick.
B_1 horizon	Darker coloured (dark grey to greyish-brown); round-topped columnar structure, the tops grey to light grey in colour. This horizon is hard and compact when dry, and is higher in clay than the A horizons; the columns break to hard angular fragmental (angular-blocky) aggregates; usually 5 to 8 in. thick, but may be up to 12 in. thick in complex podsolic-solonetzic profiles.
$B_{2(ca)}$ horizon	Variable in colour, but in present samples chiefly light yellowish-brown to olive; massive to faint columnar structures; accumulation of carbonates and sulphates; 10 to 16 in. thick. Sometimes this horizon is divided into B_2 and B_3 horizons.
C horizon	Variable in colour; massive structure; carbonates and sulphates present. Geologically the parent materials consist chiefly of thin glacial deposits overlying saline bedrock shales or of glacial till derived in part from such shales. Several profiles are developed from saline glacial-lacustrine clays.

The A horizons are moderately to strongly acid in reaction, the A_2 horizons being the most acid. The B_1 horizons are slightly acid to slightly alkaline in reaction. The $B_{(ca)}$ and C horizons are moderately to strongly alkaline.

Solodized-solonetz soils are of widespread occurrence in Saskatchewan. Because of their striking morphology, the presence of associated eroded pits (the so-called 'burn-outs' or 'blow-outs') and the particular problems related to their agricultural use, these soils have attracted more attention than have other solonetzic soils. For this reason the current studies were inaugurated with a study of soils of solodized-solonetz morphology as defined by Mitchell, Moss, and Clayton (1944), taken in all major soil zones of the province. The investigation is designed to show the similarities and differences exhibited by solodized-solonetz profiles in Saskatchewan, and ultimately to establish criteria by which they may be differentiated from other solonetzic soils.

A similar study was made of solonetz soils as defined by Mitchell *et al.* (1944). In the present paper these soils are referred to as 'solonetz-like', since they do not conform to the commonly accepted definition of solonetz soils. The term 'solonetz-like' will serve until future studies permit the adoption of a more appropriate name. A generalized description of the solonetz-like profiles is given below.

Generalized Description of Solonetz-like Profiles

A_1 horizon	The colour usually reflects the A_1 colours of the zone; columnar or cloddy, sometimes cloddy-platy structure; about 5 in. thick.
A_2 horizon	Usually absent; when present is thin, greyish coloured and platy structured, or shows merely as a slight greying at the base of the A_1.
B_1 horizon	Very dark greyish-brown, brown, or yellowish-brown; columnar (prismatic) structure, hard and compact—may show slight round-topped development; 5 to 12 in. thick.

B_2 horizon	Dark greyish-brown, light brown to light yellowish-brown; columnar structure. Frequently absent; 0 to 5 or 6 in. thick.
$B_{(ca)}$ horizon	Light brown to yellowish-brown; massive to faintly columnar; accumulation of carbonates and sulphates; 8 to 12 in. thick.
C horizon	Generally similar to parent material of solodized-solonetz, but the solonetz-like profile is also found on a wider range of parent materials.

The A_1 and B_1 horizons of the solonetz-like soils are moderately acid to neutral in reaction. The A_2 horizon, when present, is moderately to slightly acid. The B_2 horizons are slightly acid to neutral. The $B_{(ca)}$ and C horizons are moderately alkaline.

The solonetz-like soils are of widespread occurrence in Saskatchewan, occurring in all soil zones and in most of the established soil associations. Thus these soils are found not only among other solonetzic soils, but occur locally within areas of non-solonetzic soils. Because of their less striking morphology and more local occurrence they are not so readily identified in the field as are the solodized-solonetz soils.

Podzolic-Solonetzic Profile

A podzolic-solonetzic profile was included in a recent study of podzolic soils by Moss and St. Arnaud (1955). For the present study, exchangeable cations were determined on this profile. The podzolic-solonetzic profile is of interest because it possesses features of both podzolic and solonetzic soil formation. The profile includes an A_0 horizon, a very thin, platy-structured, dark grey A_1, a thick, cloddy-platy, grey A_2, and a very thick, columnar-structured B_1, of heavier texture than the A horizons. The $B_{(ca)}$ and C horizons are calcareous and saline.

Methods of Analyses

pH and conductivity were determined by the saturated soil paste and saturated soil extract methods respectively, as outlined by the United States Regional Salinity Laboratory (1954).

Exchangeable metal cations were determined by the ammonium-acetate method of Schollenberger and Dreibelbis (1930) with slight modification to adapt the method to washing by centrifuge. The modified method as used here consisted of weighing 5 g. of air-dry soil into a 100-ml. centrifuge tube; 50 ml. ammonium acetate (pH 7·0) were then added. After stirring with a rubber-tipped stirring rod the sample was allowed to stand overnight. After centrifuging on the following morning, the supernatant liquid was decanted into a filter funnel fitted with Whatman No. 40 filter paper, the filtrate being collected in a 400-ml. beaker. Another 50-ml. portion of ammonium acetate was added, the sample stirred, centrifuged, and filtered. This procedure was repeated twice more, making approximately 200 ml. of total filtrate.

Exchangeable hydrogen was determined by the method of Brown (1943), which consists essentially of calculating exchangeable hydrogen from the change in pH of the extracting solution. The filtrate was made up to a volume of 250 ml., and a 50-ml. aliquot was removed for determination of exchangeable sodium and potassium. The removal of excess

salts, and the determination of calcium and magnesium were then done by standard methods.

Calcium and magnesium were determined by standard volumetric methods for the solodized-solonetz profiles. For the solonetz-like soils the versenate method as outlined by Cheng and Bray (1951) was used.

All results are reported as milli-equivalents per 100 g. of air-dry soil.

It should be noted that the analytical results for the solodized-solonetz soils represent median values for six profiles. The results for the A_3 horizons represent two profiles only, since this horizon is not always present. Similarly, the analyses of the solonetz-like soils represent median values for ten profiles, but the results for the A_2 horizon represent four profiles only, since this horizon is not always present in these soils. Finally, the results for the B_2 horizon represent three profiles only, since this horizon may also be absent.

Results of Analyses

Solodized-solonetz soils. The analytical results for these soils are given in Tables 1 and 2. The analyses support the evidence obtained from morphological studies—that the leaching of the upper horizons has proceeded to the stage where solodization has begun. The solodic nature of these profiles is shown by the low conductivity, the relatively high acidity, and the relatively high exchangeable-hydrogen values of the A horizons. The loss of colloids, presumed to be due to solodic degradation, is shown by the low total exchange capacities of the A_2 and A_3 horizons.

The solonetzic nature of these soils is shown by the high values for exchangeable sodium in the B_1 horizons, together with the absence of exchangeable hydrogen, and the tendency for pH and conductivity values to increase in these horizons. The increase in alkalinity and soluble salts is still more apparent in the lower B horizons, but these results are not reported here.

The analyses also illustrate two other characteristic features of solonetzic soils—the presence of 10 per cent. or more of exchangeable sodium in the A_3 and B_1 horizons, and the dominance of exchangeable magnesium over exchangeable calcium in the A_2, A_3, and B_1 horizons. The exchangeable magnesium is particularly high in the B_1 horizons, where it may account for more than 50 per cent. of the total cation-exchange capacity.

The values for exchangeable potassium are highest in the A_1 horizons, where they exceed the values for exchangeable sodium. In the other horizons, however, potassium is considerably lower than sodium.

Solonetz-like soils. The analytical results for the solonetz-like soils are given in Tables 3 and 4. Comparing the results with the analysis of the solodized-solonetz profiles, the following statements may be made: in the solonetz-like soils, the B_1 horizons are less saline and slightly lower in pH values, while B_1 and B_2 horizons contain appreciable amounts of exchangeable hydrogen. The most significant difference between the two soils is the practical absence of exchangeable sodium and potassium in the solonetz-like soil. The solonetz-like profile also exhibits smaller differences in total exchange capacities between the A_2 and B_1 horizons,

TABLE 1

Median Values for pH, *Conductivity, and Exchangeable Cations in Solodized-Solonetz Soils*

Horizon	pH	*Conductivity (mmhos./cm.)*	*Total cation ex. cap.*	*Exchangeable cations (m.e. per 100 g. of soil)*					*% Na of total ex. cap.*
				Ca	Mg	Na	K	H	Ca/Mg	
A_1 . .	5·7	0·3	19·19	8·08	4·06	0·44	0·95	6·76	1·71	2·33
A_2 . .	5·4	0·4	12·78	3·22	4·06	0·69	0·23	4·51	0·73	6·68
B_1 . .	6·9	1·8	28·68	6·47	15·44	3·82	0·59	..	0·40	13·97

TABLE 2

Range of Values for pH, *Conductivity, and Exchangeable Cations in Solodized-Solonetz Soils*

Horizon	pH	*Conductivity (mmhos./cm.)*	*Total cation ex. cap.*	*Exchangeable cations (m.e. per 100 g. of soil)*					*% Na of total ex. cap.*
				Ca	Mg	Na	K	H	Ca/Mg	
A_1 . .	5·4–6·1	0·2–0·4	17·9–37·1	6·2–16·8	3·7–11·6	0·3–1·2	0·9–1·3	2·6–12·1	0·9–2·6	1·6–3·2
A_2 . .	5·0–5·8	0·3–0·8	12·4–15·7	1·5–7·3	3·3–5·6	0·6–2·3	0·2–0·6	2·3–5·0	0·3–1·5	4·4–25·6
A_3 . .	6·1–6·2	0·5–1·0	7·7–10·3	2·2–3·1	3·1–5·4	1·0–1·2	0·2–0·4	0·5–1·1	0·6–0·7	9·8–17·7
B_1 . .	6·7–7·6	0·7–11·3	20·0–35·8	2·3–12·0	13·1–20·4	3·6–11·2	0·5–1·0	..	0·2–0·6	10·6–40·2

TABLE 3

Median Values for pH, *Conductivity, and Exchangeable Cations in Solonetz-like Soils*

Horizon	pH	*Conductivity (mmhos./cm.)*	*Total cation ex. cap.*	*Exchangeable cations (m.e. per 100 g. of soil)*				
				Ca	Mg	Na	K	H	Ca/Mg
A_1 . .	6·41	0·40	24·34	11·72	8·11	Tr.	Tr.	6·30	1·24
A_2 . .	5·70	0·35	22·43	5·53	9·14	,,	,,	4·50	0·73
B_1 . .	6·48	0·27	25·86	11·40	11·85	,,	,,	5·40	0·96
B_2 . .	6·92	0·45	28·14	11·17	9·94	,,	,,	4·05	0·86

TABLE 4

Range of Values for pH, *Conductivity, and Exchangeable Cations in Solonetz-like Soils*

Horizon	pH	*Conductivity (mmhos./cm.)*	*Total cation ex. cap.*	*Exchangeable cations (m.e. per 100 g. of soil)*					
				Ca	Mg	Na	K	H	Ca/Mg
A_1 . .	5·8–7·2	0·3–0·6	19·9–27·7	5·8–19·0	5·1–11·6	Tr.	Tr.	1·3–9·0	1·1–2·6
A_2 . .	5·6–6·5	0·3–0·4	17·8–27·9	4·3–11·0	7·7–13·3	,,	,,	3·6–9·0	0·5–0·8
B_1 . .	5·9–7·2	0·2–0·9	23·2–35·4	7·6–17·7	6·6–18·1	,,	,,	0·9–10·3	0·5–2·1
B_2 . .	6·5–7·3	0·3–0·5	18·6–31·9	7·8–16·1	8·2–12·9	,,	,,	0·9–7·7	0·8–2·0

and only in the A_2 horizon does exchangeable magnesium clearly exceed exchangeable calcium. Exchangeable magnesium predominates in the B_1 horizons of approximately half of the profiles studied.

TABLE 5

pH, *Conductivity, and Exchangeable Cations in a Podzolic-Solonetzic Soil*

Horizon	pH	Conductivity (mmhos./cm.)	Total cation ex. cap.	Exchangeable cations (m.e. per 100 g. of soil)						% Na of total ex. cap.
				Ca	Mg	Na	K	H	Ca/Mg	
A_1	6·4	0·4	33·78	20·7	6·98	0·52	0·80	4·73	2·97	1·79
A_2	5·8	0·3	27·33	12·7	8·98	0·64	0·55	4·50	1·41	2·80
B_1	4·8	0·3	35·33	15·3	12·60	1·13	0·68	5·63	1·22	3·80

The foregoing comparisons suggest that the solonetz-like soils show less evidence of solonetz development than do the solodized-solonetz soils.

Podzolic-solonetzic soils. The analysis of this soil is given in Table 5. The results show that the B_1 is more acidic than the A_1 and A_2 horizons, and that exchangeable calcium exceeds exchangeable magnesium in all three horizons. These features are common to the grey wooded (podzolic) soils of Saskatchewan.

The values for exchangeable sodium, although small, are greater than those reported for podzol and podzolic soils (U.S.D.A., 1952). The lower B and C horizons of the podzolic-solonetzic profile are saline, as shown by conductivity values of 4 to almost 7 mmhos./cm. This salinity and the structure of the B_1 horizon are features common to the solonetzic soils.

Discussion

The genesis and classification of solonetzic soils have been discussed by Vilenski (1928), Nikiforoff (1930), Kelley (1934), Kellogg (1934), Rost (1936), Joffe (1936), Burvill and Teakle (1938), Byers *et al.* (1938), de Sigmond (1938), and many others. More recent studies are reviewed in *Soils and Fertilizers* (1951). Among the problems dealt with by these authors, none has caused more discussion than the question of whether solonetzic soils should be defined by morphological or by chemical characteristics. After perusing the literature one is tempted to add that no problem in soil classification has caused more confusion. The actual fact is that few if any soils can be completely identified and described by one set of criteria alone. Furthermore, where soil classification is designed primarily to guide soil-survey work, as in Saskatchewan, information from both field and laboratory is required to establish a practical system of classification.

Saskatchewan workers are therefore interested in a system of classification which will permit them to identify and map soils in the field. They are also interested in laboratory studies which help to determine the validity of the field classifications. On this basis the aim of the present

studies is to relate the profile characteristics recognized in the field to the composition of the profile as determined in the laboratory.

The solodized-solonetz soils of the present study are identified by morphological features which can be recognized in the field, and which are also associated with certain chemical and physical properties. Among the latter are the acid, non-saline conditions in the A horizons, the presence of 10 per cent. or more of exchangeable sodium in the A_3 and B_1 horizons, and low ratios of exchangeable Ca/Mg in the A_2, A_3, and B_1 horizons. Similar results have been reported from other studies of solodized-solonetz soils of Saskatchewan (Mitchell and Riecken, 1937; Janzen, 1941; Riecken and Stalwick, 1946; Bentley and Rost, 1947).

The solonetz-like soils, with their less striking morphology, are characterized by the practical absence of exchangeable sodium, and the dominance of exchangeable calcium and magnesium. The exchangeable Ca/Mg ratios of the B_1 horizons are close to 1, and the lowest ratios are found in the A_2 horizon. This horizon also shows the lowest pH values. However, since the A_2 is not always present it cannot be regarded as a characteristic horizon in these profiles.

The foregoing discussion indicates that 10 per cent. or more of exchangeable sodium and a dominance of exchangeable magnesium over exchangeable calcium are characteristic of Saskatchewan soils possessing leached A horizons and well-developed greyish, round-topped columnar B_1 horizons. With little or no exchangeable sodium, and with slight or no predominance of exchangeable magnesium over calcium, the soils lack the well-developed round-topped columnar B_1, and the A_2 horizon is absent or relatively thin. It would appear, therefore, that about 10 per cent. of exchangeable sodium is a significant value in characterizing the soils described in Saskatchewan as solodized-solonetz. This value of 10 per cent. exchangeable sodium has been correlated with the poor physical conditions associated with solodized-solonetz soils (Riecken and Stalwick, 1946). de Sigmond (1938) in discussing salty alkali soils, stated that when sodium exceeded 10–15 per cent. of the total metallic cations absorbed (S value) the dispersing effect of the sodium cations became appreciable. It is of interest to note that de Sigmond expresses the sodium as per cent. of the basic cations, and not of the total exchange capacity.

The significance of exchangeable magnesium is not so apparent. It would appear that high values for exchangeable magnesium occur in B_1 horizons possessing the higher values for exchangeable sodium. This relationship was suggested by Bentley and Rost (1947), and is also illustrated by the present study, in the analyses of the solodized-solonetz B_1 horizons given in Tables 1 and 2.

Riecken (1944) showed that both the adsorption and retention of exchangeable magnesium by B horizons of selected soils were favoured by alkaline conditions. Thus at pH values of 8·15 and higher, more magnesium than calcium was adsorbed by a sodium clay from a system containing equal concentrations of Ca and Mg ions; in another soil, using NaOH–NaCl as replacing electrolyte, less magnesium than calcium was released when the pH reached 8·7; at pH values above 9·0 all exchangeable magnesium was retained.

On the basis of the above experiments, the high proportion of exchangeable magnesium in the solodized-solonetz soils may be explained on the assumption that these soils have developed from alkali-solonetz profiles. In Saskatchewan the latter soils are characterized by pH values of 8·0 to 9·6, which according to Riecken's results would favour the accumulation of magnesium. Furthermore, according to Pankov and Shavryguin, as quoted by Bentley and Rost (1947), the exchangeable magnesium of the B_1 horizon first increases as solodization proceeds, and then decreases. The latter authors showed that in solodi profiles of Saskatchewan exchangeable magnesium is lower than exchangeable calcium.

The occurrence of considerable exchangeable magnesium in solonetzic soils has also been reported by Sushko (1933), Ellis and Caldwell (1935), Teakle (1953), and others.

The field and laboratory studies reported above suggest that the solodized-solonetz and the solonetz-like soils differ sufficiently from each other to justify their separation as distinct genetic profiles. It is not yet clear, however, whether or not they represent stages in the same soil-forming process. It does not seem likely that the solonetz-like profile could develop into the solodized-solonetz, unless additional sodium and possibly other salts were introduced into the soil. It is still more difficult to imagine the solodized-solonetz profile altering to the solonetz-like. It is obvious that more work is required on all soils of the solonetzic group in this region before it becomes possible to do more than speculate about their genesis.

The present studies, although limited, also suggest that the podzolic-solonetzic soils are correctly designated as complex profiles showing some features of both podzolic and solonetzic development.

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THE EFFECT OF EARTHWORMS ON THE DISPERSAL OF SOIL FUNGI

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Introduction

THERE has been much work on the effect of earthworms on soil structure and fertility, and a more limited study of the effect on the soil flora of passage through the earthworm's alimentary canal. Bassalik (1913) found no qualitative difference between the bacterial and fungal flora of the alimentary canal, of the earthworm casts, and of the surrounding soil in which the earthworms were living, but Aichberger (1914) reported that on passage through the canal there was a differential killing of organisms which had no protective cell wall. Stöckli (1928) found that the flora of the canal and of the surrounding soil was qualitatively similar, but that there was a great increase in the total number of organisms present in the canal, and an increase in the relative proportions of pectin-splitting fungi. More recently Dawson (1948) stated that the numbers of bacteria were reduced by passage through the canal while the numbers of fungi were unaffected, and Day (1950) found that while the total numbers of bacteria, actinomycetes, and fungi were 'not consistently greater or less' in fresh casts of *Lumbricus terrestris* Linn. than in the surrounding soil, there was a difference in the proportions of species present. In particular he found no change in the number of nitrifying bacteria, but that passage through the canal reduced the number of *Bacillus cereus* var. *mycoides* while *Serratia marcescens* was killed out completely, apparently by the action of some pharyngeal secretion. He also pointed out that the design of the earlier experiments was inadequate to determine changes in the numbers and proportions of different species in the population resulting from passage through the canal, which may explain some of the discrepancies between the published reports.

In these investigations work was concentrated on the examination of bacterial activity, and the fungi generally received more cursory attention. In particular there was no examination of the effect of the presence of earthworms on the rate of spread of fungi through the soil. The work has shown that at least some fungal spores can survive passage through the alimentary canal, and that there may be some differential killing of the species of the original population. It is also probable that the earthworm will bear a surface contamination of spores and mycelial fragments, and that these combined characters may make it an important factor in fungal dispersal. The following investigation was therefore designed to study (*a*) the living fungal flora of some typical earthworm alimentary canals; (*b*) the effect of the presence of earthworms on the rate of spread of some selected fungi through a sterilized soil.

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Methods

(*a*) *Isolation of fungi from the alimentary canal*

Specimens of *Lumbricus terrestris* Linn. were collected from the grounds of the University of Glasgow and of the West of Scotland Agricultural College, Auchincruive, Ayr. They were washed with tap water immediately after collection to remove macroscopic surface debris, and then killed by immersion in 0·1 per cent. mercuric chloride. The mercuric chloride was washed off with sterile distilled water, and portions of the contents of all parts of the alimentary canal were removed by sterile dissection. The samples were plated on to malt-extract agar, potato-dextrose agar (Ainsworth and Bisby, 1950), and peptone-glucose agar (eupeptone 0·5 g., glucose 1·0 g., agar 2·0 g., distilled water 100 ml.), all of which were adjusted to pH 4·0 to depress bacterial growth. Isolations were made of all fungi which developed.

(*b*) *Examination of the effect of earthworms on fungal spread*

Four species of fungi isolated from the alimentary canals of *Lumbricus terrestris* were used for these tests. Three of these (*Rhizopus nigricans*, *Trichoderma viride*, *Penicillium spinulosum*) occurred very frequently in the worms examined. The fourth, which was isolated only once, was a *Cephalosporium* (CMI 58654) with thin-walled spores. A 3 in. layer of garden loam was placed in each of twelve wooden boxes measuring 3 ft. × 8 in. × 6 in. Each box was covered with a loosely fitting glass sheet, and the whole autoclaved at 20 lb. pressure for 1 hour on each of two successive days. In eight of the boxes 100 ml. of a mixed spore suspension of the four test fungi was then thoroughly mixed with a sample of the soil. The inoculated sample was replaced so that it formed a vertical band approximately 1 in. across, occupying the whole of a vertical cross-section of the soil approximately 6 in. from one end. In four of these inoculated boxes fifteen specimens of *Lumbricus terrestris* were then placed in a hollow in the soil between the fungal inoculum and the nearest end of the box. The remaining four uninoculated boxes were held unopened as a control. The boxes were stored in a random pattern on the floor of the laboratory at room temperature. Samples of soil were removed, by use of a sterile cork borer, from three evenly spaced sites between the inoculum and the far end of the box at 48-hour intervals. The samples were plated on 2 per cent. malt agar and incubated at 24° C. to determine whether the test fungi were present in them.

Results and Discussion

1. *Flora of the alimentary canal*

The species of fungi found in the ten earthworms examined are detailed in Table 1.

TABLE 1

Isolations of Fungi from the Alimentary Canal of Lumbricus terrestris *Linn.*

Specimen	*Locality in which collected*	*Date of collection*	*Part of specimen examined*	*Species*	*Relative thickness of spore wall*	Isolate A, CMI 59214	*Verticillium* sp.	*Torula* sp.	*Trichoderma viride*	*Penicillium* sp. (*Verticatum* series)	*Penicillium Verticatum*	*Penicillium* sp. (*digitatum* series)	*Penicillium spinulosum*	*Rhizopus nigricans*	*Pythium* sp.	*Mucor* sp.	*Gliocladium* sp. (*roseum series*)	*Gliocladium roseum*	*Fusarium culmorum*	*Cladosporium cladosporioides*	*Cephalosporium* sp. CMI 58654	*Cephalosporium* sp.
					Thin		*Thin*	*Thick*	*Thin*	*Thin*	*Thin*	*Thin*	*Thin*	*Thick*	*Thin*	*Thick*	*Thin*	*Thin*	*Thin*	*Thick*	*Thin*	*Thin*
1	Univ. Glasgow	15 Oct. 54	alim. canal				×	×	×	×	×	×		×	×	×		×		×		×
2	,,	2 Nov. 54	,,				×		×	×		×	×	×		×	×					
3	,,	12 Nov. 54	,,				×	×	×	×			×	×	×	×		×				
4	,,	27 Nov. 54	,,						×				×	×		×		×	×			
5	Auchincruive	5 Dec. 54	,,			×	×		×		×			×	×					×		
6	,,	7 Dec. 54	,,				×		×				×	×	×	×						
7	,,	12 Dec. 54	,,				×		×	×				×	×	×						
			rectum																			
8	,,	17 Dec. 54	alim. canal				×		×			×		×						×		
9	,,	22 Dec. 54	,,				×	×	×					×					×	×		
			rectum																			
10	Univ. Glasgow	28 Dec. 54	alim. canal				×		×					×								

These results show that a substantial number of viable fungal spores can be isolated from the intestine, including species of both thick-walled and thin-walled spore types. The limited number of species found may be associated with the smallness of the sample, with a selective effect of the method of isolation, or with a selective effect of the action of the passage through the canal on the viability of different spores ingested. It may be noted that although only a small number of species were isolated some of these were found consistently in worms from different areas at different times of the year. The smaller number of isolates found in midwinter compared with those found in the late autumn agrees with the findings of Stöckli (loc. cit.) who reported an increase in the microbiological flora of the soil in April–June and in September–November. The rectal end of the intestine was examined separately in two worms, and found to contain much the same species as the rest of the alimentary canal. This indicates that there was no complete killing of these species as they passed down the canal, but it does not give any information of any possible quantitative selective killing which may have occurred.

2. *Examination of the effect of the earthworm on fungal spread*

Table 2 shows that the rate of spread of the test fungi was greatly increased in the boxes in which earthworms were present. It was noted in particular that in boxes 2 and 4 the earthworms appeared on the surface within a few minutes of being placed in the soil, and that within half an hour they were present at the end of the box distant from the inoculum. Though the soil was initially disinfested by autoclaving there were opportunities for it to become reinfested by air-borne spores during the experimental sampling, &c., and the earthworms used were not disinfested before being placed in the soil. As a result several other species of fungi were isolated from the test plates, particularly species of *Penicillium*. Their occurrence is not recorded, as the complete absence of the test fungi from the control boxes and their regular spread from the site of inoculum in the inoculated boxes without worms shows that the rapid spread in the other boxes is not due to the presence of secondary contaminants.

These results show that the activity of earthworms may have a very significant effect on the distribution of the soil fungi. It would be desirable to carry out more work to examine the possibility of their having a selective effect, and to examine their effect in different soil types and conditions. It is uncertain whether one of the authors (M. K.) will be able to carry out further work on his return to Egypt, however, and the results are thought to be of sufficient interest to be published in their present form.

Summary

1. Viable spores of species of fungi with both thin-walled and thick-walled spores can be recovered from the alimentary canal of *Lumbricus terrestris* Linn.

2. The rate of spread of four test species of fungi in a sterile soil was very substantially increased when earthworms were present.

TABLE 2

The Effect of the Presence of Lumbricus terrestris *Linn. on the Distribution of Fungi*

(The initials represent the recovery of *Cephalosporium* sp. (C), *Penicillium spinulosum* (P), *Rhizopus nigricans* (R), and *Trichoderma viride* (T), from the sites indicated.)

	Inoculated soil with earthworms present										*Inoculated soil with no earthworms*										*Control*																			
Box	1			2			3			4			5			6			7			8			9			10			11			12		
Sample site	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Days: 2	C	C	:	C	C	:	:	:	:	C	C	C	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	P	:	:	P	P	:	:	:	:	P	P	P	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	:	R	:	R	R	:	:	:	:	R	R	R	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	:	:	:	T	T	:	:	:	:	T	T	T	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
4	C	C	C	C	C	C	:	:	:	C	C	C	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	P	P	:	P	P	P	:	:	:	P	P	P	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	:	:	R	R	R	R	:	:	:	R	R	R	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	:	:	:	T	T	T	:	:	:	T	T	T	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
6	C	C	C	C	C	C	C	C	C	C	C	C	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	P	P	:	P	P	P	P	P	P	P	P	P	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	R	R	R	R	R	R	R	R	R	R	R	R	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	:	:	:	T	T	T	:	:	:	T	T	T	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
8	C	C	C	C	C	C	C	C	C	C	C	C	C	:	:	C	:	:	:	:	:	C	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	P	P	P	P	P	P	P	P	P	P	P	P	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	R	R	R	R	R	R	R	R	R	R	R	R	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	T	T	T	T	T	T	T	T	T	T	T	T	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
10	C	C	C	C	C	C	C	C	C	C	C	C	C	:	:	C	:	:	C	:	:	C	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	R	R	R	R	R	R	R	R	R	R	R	R	P	:	:	P	:	:	P	:	:	P	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:
	T	T	T	T	T	T	T	T	T	T	T	T	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:	:

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THE INFLUENCE OF VARIOUS ROTATIONS ON COARSE-TEXTURED SOILS AT CHAPMAN AND WONGAN HILLS RESEARCH STATIONS, WESTERN AUSTRALIA

I. NITROGEN AND ORGANIC-CARBON CONTENTS OF THE SOILS

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Summary

The effect of four wheat rotations on soil organic carbon and nitrogen in two long-term experiments at Chapman and Wongan Hills Research Stations is discussed. The experiments compare continuous wheat, fallow–wheat, fallow–wheat–pasture, and fallow–wheat–2 years lupins.

On the assumption that adjacent uncultivated soils were comparable in carbon and nitrogen to the original virgin soils, the four-course rotation is at each site the only one which maintained soil nitrogen at levels approaching those of the virgin soils. The two- and three-course rotations, including in each case a year of fallow, by contrast, produced serious losses in both carbon and nitrogen at both localities, but particularly at Chapman. The soil-nitrogen data support the hypothesis of Shier and Cullinane (1948) that these levels are influencing wheat yield and the flour quality of the grain.

The data emphasize, also, the very low nitrogen and carbon contents of these soils both in the virgin condition and after 22 years of a four-course rotation in which half of each 4-year period was occupied by a leguminous crop.

It is concluded that much longer periods under legumes are necessary if the carbon and nitrogen levels of these soils are to approach those typical of known highly fertile soils elsewhere.

Introduction

EARLY agricultural development in Western Australia was largely confined to the finer-textured soils characteristic for the most part of the broad valleys of the wheat-belt. These soils have pedogenic affinities with the wheat-growing red-brown earths and solonized brown soils of eastern Australia. Their content of nitrogen and other plant nutrients, with the exception of phosphorus, is such as to confer moderate fertility on them (Teakle, 1938). These soils are limited in extent compared with the large areas of sandy laterites and other coarse-textured soils, which according to Smith (1952) constitute no less than two-thirds of the whole south-western agricultural region of the state. This region is bounded on the west by the coast and on the east by the 12-in. rainfall isohyet. The successful utilization of these coarse-textured soils is clearly, therefore, of the utmost importance to the agricultural development of the region. These lateritic 'sandplain' soils are of extremely low inherent fertility; in fact, it is considered that in the virgin state they are lower in nitrogen, organic matter, and phosphorus than any other soils in the world used extensively for the growing of wheat. Total soil–nitrogen values as low as 0·03–0·05 per cent. are frequent in these soils.

The traditional rotation for the Western Australian wheat belt has been the three-course, fallow–wheat–stubble or volunteer-pasture practice. The proportion of fallow, wheat, and sown pasture in a 40 per cent.

sample of the total cleared area for two statistical regions of the wheat-belt is presented in Table 1.

TABLE 1

Land Use in the W.A. Wheat Belt (1950–1)*

Statistical region	*% area under fallow*	*% area under wheat*	*% area under sown pasture*	*% remainder†*
Northwestern . .	22·6	27·5	8·8	41·1
Southwestern . .	17·2	24·3	7·5	51·0

* Data from Statistical Register of W.A. (1950–1).

† Remainder includes newly cleared land prepared for next season, grazing, volunteer pasture, and other crops (oats, barley, &c.).

The volunteer pasture consists principally of annual grasses (*Bromus* spp., *Festuca* spp., and *Hordeum* spp.), capeweed (*Cryptostemma calendula* (Linn.) Druce), and *Erodium* spp., with few, if any, leguminous species. The sown pasture is normally dominated by subterranean clover (*Trifolium subterraneum* L.).

The economic development of the lateritic sandy soils is dependent on the use of crop or pasture legumes, especially subterranean clover, in rotations with cereal crops so that the nitrogen and organic-matter status of these soils is raised. For this purpose, adequate applications of phosphorus as superphosphate are uniformly necessary and in some areas treatment of the soils with trace elements, particularly copper and zinc, is also required. Ample indirect evidence that the inclusion of a legume in the rotation maintains or improves soil fertility has been obtained by farmers and from the results of experiments carried out by the State Department of Agriculture. These have been reviewed by Underwood (1951), although in general only the effect of various rotations on wheat yield and grain quality has been measured. Striking increases in wheat yields and grain quality have been reported from Chapman and Wongan Hills as a result of including legumes in a rotation on coarse-textured and lateritic soils (Shier and Cullinane, 1948), but the changes which may occur in these soils following the different rotational practices were not measured. The present study is designed to fill this gap as part of a wider investigation of the nitrogen economy of the soils of the wheat-belt of Western Australia.

Materials and Methods

(*a*) *Localities*

With the permission of the W.A. Department of Agriculture soil samples (0–4 in.) were taken from wheat-rotation experiments at Chapman and Wongan Hills Research Stations.

Chapman is situated 28 miles north of Geraldton and has an average annual rainfall of 18·27 in. Smith (1952) has classified the soils in this area as non-calcic red and brown soils. The surface horizon is a red-brown sandy loam, the texture becoming finer with depth. The surface

soil has a pH of 6·5. In the virgin condition the soil type carries *Acacia acuminata* Benth. and *Eucalyptus foecunda* Schauer woodland.

Wongan Hills is 120 miles north-east of Perth, with an annual average rainfall of 14·29 in., is situated on a relict lateritic sandplain the surface of which is a non-gravelly grey-brown loamy sand. The sandy surface has a pH of 6·5, and passes into a yellow-brown loamy sand overlying a laterite horizon, beneath which there is kaolin.

The mechanical analyses of the two soils are very similar, as is shown in Table 2.

TABLE 2

Mechanical Analyses of Chapman and Wongan Hills Soils. International System

Locality	% *coarse sand*	% *fine sand*	% *silt+clay*	% *sesquioxides*
Chapman . . .	50·1	37·1	11·2	0·13
Wongan Hills . .	55·5	34·8	12·1	0·18

(*b*) *Experimental*

The experiments were established in 1929 and compare the following four rotations:

(i) Continuous wheat;
(ii) Fallow–wheat;
(iii) Fallow–wheat–volunteer pasture;
(iv) Fallow–wheat–lupins–lupins.

Both experiments consist of 20 plots laid side by side. Ten of these represent each phase of the one-, two-, three-, and four-course rotations; these are then repeated. Each plot measures 10 chains long and 1 chain wide and occupies an area of one acre.

Fifteen random soil samples were obtained from each of the 20 plots and each 15 were composited into 1.

Organic carbon (Walkley, 1935) and organic nitrogen (Willits, Coe, and Ogg, 1949) were determined on the $< 2{\cdot}0$-mm. fraction of each sample. The organic-carbon data shown below have not been converted to organic-matter equivalent.

Results

(*a*) *Chapman Research Station*

The carbon, nitrogen, and wheat-yield data for the 1953 sampling of the 20 plots are shown in Table 3.

The fallow–wheat–lupins–lupins and the continuous-wheat rotations are the only rotations which have maintained soil carbon and nitrogen close to that of the virgin soil. The data for virgin soil were obtained from samples between the trial and the fence-line that had not been cultivated. It is more than probable that fertility has been maintained on the continuous-wheat treatment by the absence of fallow and consequent imperfect weed control. It should be pointed out also that these plots

supported a good stand of *Medicago denticulata* Willd. at sampling time. Experience at Werribee and Rutherglen (Penman, 1949) and at Rothamsted (Report, 1947) has also indicated that continuous-wheat treatments have a carbon and nitrogen status comparable to the virgin soil sampled at the beginning of the experiment.

TABLE 3

Chapman Research Station
Wheat-rotation Experiment. Soil Data (0–4 in.) and Wheat Yields, 1953

Rotation	% *nitrogen*	% *organic carbon*	*Wheat yields (1936–51) (bu./acre)*
1. Continuous wheat . .	0·042	0·40	5·3
2. Fallow–wheat . . .	0·021	0·24	8·1
3. Fallow–wheat–pasture . .	0·027	0·27	11·4
4. Fallow–wheat–lupins–lupins .	0·040	0·41	15·9
Virgin soil (around fence line) .	0·053	0·53	..

Both the fallow–wheat and fallow–wheat–pasture rotations are significantly lower (0·1 per cent. level) in carbon and nitrogen than the four-course rotations. Fallow-wheat is also significantly lower (5 per cent. level) in nitrogen than the fallow–wheat–pasture rotation, but not in carbon content. The relevant analyses of variance have been presented elsewhere (Drover, 1954).

(*b*) *Wongan Hills*

The carbon and nitrogen data from the same experimental layout located at Wongan Hills are presented in Table 4.

The soil nitrogens are very similar to those at Chapman, except in the continuous-wheat and 'virgin' soils. The nitrogen content of the soil under continuous wheat is not comparable with that of the four-course rotation as at Chapman, and the nitrogen content of the 'virgin' soil is half that at Chapman. In addition, the C:N ratios of the soils tend to be wider at Wongan Hills. The wheat yields are also higher than those from Chapman.

TABLE 4

Wongan Hills Research Station
Wheat-rotation Experiment. Soil Data (0–4 in.) and Wheat Yields, 1951

Rotation	% *nitrogen*	% *organic carbon*	*Wheat yields (1936–51) (bu./acre)*
1. Continuous wheat . .	0·025	0·35	4·6
2. Fallow–wheat . . .	0·021	0·27	13·0
3. Fallow–wheat–pasture . .	0·028	0·35	17·2
4. Fallow–wheat–lupins–lupins .	0·037	0·49	22·3
Virgin soil (around fence line) .	0·027	0·50	..

The fallow–wheat–2 years lupins rotation has maintained soil nitrogen above the level of the 'virgin' soil in contrast to Chapman. The tendency for fallow–wheat–pasture to maintain soil nitrogen at this locality is also in marked contrast to Chapman.

Soil from the four-course rotation is significantly (at the 0·1 per cent. level) higher in both carbon and nitrogen than soil from the two- and three-course rotation. The continuous-wheat soil is at the same nitrogen level as the 'virgin' soil, but is considerably lower in carbon. The fallow–wheat rotation is the only one to show a loss of soil nitrogen.

(*c*) *The nature of the soil-organic matter*

The analytical results from Chapman and Wongan Hills are interesting in view of the differences in locality, fertility status of the virgin soil type and wheat yield, and the similarity in the present nitrogen and organic-matter content of the soils. On the assumption that the uncultivated soil around each trial is of comparable nitrogen content to the original virgin soil, then, with the exception of the continuous-wheat rotation, the remaining three rotations have changed soil nitrogen to approximately the same respective levels at both localities. The higher nitrogen content under continuous wheat at Chapman is considered to be due to the presence of *Medicago* spp.

In spite of these facts the average wheat yields have been about 40 per cent. lower at Chapman than at Wongan Hills. The rather anomalous results led to an investigation into the nature of the soil-organic matter at these two localities.

Norman (1942) has stressed the need for information on the basic chemical differences between types of organic matter. As a means to this end, Norman suggests the use of the hypoiodite oxidation of lignin in the soil-organic matter. Moodie (1950) has proposed a suitable method for this determination and it has been adopted here. The results are presented in Table 5.

TABLE 5

Hypoiodite Reactivity—Chapman and Wongan Hills Rotation Experiments

Rotation	*Iodine uptake* (*m.e.* I_2/*g. carbon*)	
	Chapman	*Wongan Hills*
1. Continuous wheat	18·1	23·3
2. Fallow–wheat	18·0	24·2
3. Fallow–wheat–pasture	18·5	21·8
4. Fallow–wheat–lupins–lupins	20·3	20·9

Analysis of variance (Drover, 1954) showed that there was no significant difference between treatments, within treatments, and between blocks at each locality. In other words, there is no significant difference in the composition of organic matter under the four rotations as measured by the hypoiodite reactions.

When a comparison is made, however, between the iodine uptake at both localities Wongan Hills is significantly higher in iodine uptake than

Chapman (5 per cent. level). Norman and Moody (1940) have compared two soils with similar organic-carbon contents and have obtained differences in iodine uptake which were related to a lower biological reactivity in the soil with the lesser iodine uptake. This finding, if applicable to the two soils discussed here, would indicate that the lower wheat yields at Chapman may be related to a more resistant type of organic matter at this locality. Nevertheless, further research into the composition of soil-organic matter is required, particularly as higher wheat yields were obtained under conditions of lower rainfall. It is realized that other factors, such as greater leaching losses of nitrate during the early winter months at Chapman, may operate.

Discussion

The yields and flour strength of the wheat from these experiments at Wongan Hills and Chapman have been discussed by Shier and Cullinane (1948). The wheat yields increase with the widening of the rotation. Flour strength and protein values increase similarly. Shier and Cullinane suggested that these increases were largely the result of an improvement in the nitrogen status of the soil following the legume pasture in the four-course rotation. The soil data just presented confirm this hypothesis at both localities.

The very low fertility of the soils must be stressed, both in the virgin state and after 22 years of a four-course rotation in which half of each 4-year period was occupied by a leguminous crop. Hallsworth (cit. Forster, 1950) considered that soils with 0·032 and 0·049 per cent. nitrogen were 'wheat sick' in northern New South Wales. But the nitrogen levels at Chapman and Wongan Hills ranged between 0·021 and 0·053 per cent. Further, the losses in carbon and nitrogen are of a much greater order than those reported by Penman (1949) for comparable rotations in Victoria and those of Hallsworth *et al.* (1954) in northern New South Wales, which refer to quite fine-textured soils. There is considerable evidence that the presence of clay in a soil is necessary to fix and hold the soil-organic matter and associated nitrogen against rapid decomposition by the soil micro-organisms. Such evidence has been obtained by Allison *et al.* (1949) and Ensminger and Gieseking (1942).

Fallow–wheat and fallow–wheat–pasture rotation effected a marked decline in soil nitrogen and carbon, particularly at Chapman, and it is concluded that this decline would have occurred on similar soils elsewhere with similar cropping practices. Either much longer periods under legumes are necessary if the carbon and nitrogen levels of these soils are to be raised anywhere near those of known highly fertile soils elsewhere, or their texture limits them to relatively low levels of these constituents.

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THE INFLUENCE OF VARIOUS ROTATIONS ON COARSE-TEXTURED SOILS AT CHAPMAN AND WONGAN HILLS RESEARCH STATIONS, WESTERN AUSTRALIA

II. SOME PHYSICAL CHARACTERISTICS OF THE SOILS

K. NEWTON AND D. P. DROVER

Summary

The effect of four wheat rotations on the water stability of the aggregates, organic carbon, porosity relations, and depth of penetration of a penetrometer at Chapman and Wongan Hills Research Stations is discussed. These rotations compare continuous wheat, fallow–wheat, fallow–wheat–pasture, and fallow–wheat–2 years lupins. The soils are coarse-textured.

Significant correlations were obtained between several measurements of structure. These include organic carbon and aggregation, organic carbon, and capillary porosity. Non-capillary porosity is correlated with penetrometer readings. No such relation was found with total porosity.

Wetting and drying of the soil and the action of growing plant roots are considered the two main factors contributing to the physical condition of the soil, and fallowing is considered to be the principal agent causing loss of structure.

Water-stable aggregates were demonstrated in the lateritic sandplain soils from Wongan Hills. These soils have been usually regarded as structureless. Variations in the content of coarse sand considerably obscured the results from this locality.

Introduction

In a previous paper (Drover, 1956) it has been shown that the soil content of organic carbon and nitrogen of a fallow–wheat, fallow–wheat–pasture, and a fallow–wheat–2 years lupins rotation increased with the length of the rotation at Chapman and Wongan Hills. At Chapman, a continuous-wheat rotation had a slightly lower fertility status than the four-course, which was believed to be due to lack of fallow and a good stand of *Medicago* spp. associated with a poor wheat crop. At Wongan Hills, on the other hand, in the absence of any such legume the continuous-wheat was much lower in carbon and nitrogen than the four-course rotation.

To examine more closely the effect of rotation on soil fertility a study of some of the physical characteristics of these two soils was made. Drover (1954) has shown that at Chapman the wheat phase of the four-course rotation had a significantly lower percentage disaggregation than the wheat phase of the fallow–wheat and fallow–wheat–pasture rotations. The four-course rotation also had the highest proportion of aggregates > 4·0 mm. diameter. These data are shown in Table 1.

In other parts of Australia it has been shown that soil structure declines under short rotations (Stephens *et al.*, 1945; Clarke and Marshall, 1947; Woodruffe, 1949). Longer rotations, on the other hand,

particularly those including legumes, have tended to maintain or improve soil structure (Downes and Leeper, 1940).

TABLE 1

*Per cent. Disaggregation and per cent. Particles > 4·0 mm. Wheat Treatments, Chapman, 1953**

	Continuous wheat	*Fallow–wheat*	*Fallow–wheat–pasture*	*Fallow–wheat–lupins–lupins*
% Disaggregation . .	478·45	623·38	526·41	421·58
% Particles > 4·0 mm. diameter . . .	135·12	93·19	131·87	186·84

* All observations sum of 16 observations:

	Disaggregation	*Particles > 4·0 mm.*
L.S.D. for . .	5%—123·51	5%—55·88
	1%—177·62	1%—80·36

Materials and Methods

(*a*) *Localities*

Soil samples (0–3·5 in.) were taken from the wheat-rotation experiments at Chapman and Wongan Hills Research Stations. The rotations are described in a previous paper (Drover, 1956) together with a brief account of the climate and soils of these research stations.

(*b*) *Sampling*

At Chapman soil sampling was carried out between 31 August and 1 September 1954 when the wheat plants were about 24 in. high but were not flowering. As the soil was moist when sampled and air-dry when analysed the percentage aggregation measured may be slightly higher than actual, due to the cementation effects produced by drying.

At Wongan Hills the samples were taken on 9 August 1954, at which time the samples were moist, but they were air-dry when the analyses were made. Unfortunately, the pasture plots of the 1953 treatments which were to be fallowed in 1954 had not been given this treatment, neither had the 1953 wheat plots been sown to pasture.

For the aggregation and organic-carbon analyses, 8 random samples were taken over each plot. Similarly, for porosity measurement, 8 samples were taken over each of the 20 plots, but these were taken adjacent to the samples taken for the aggregation and carbon analyses so that correlation of measurements would be justified.

Penetrometer readings were taken in the field, 12 or 14 observations being made at random over each plot.

(*c*) *Measurement of water-stable aggregates*

A Coile (1936) constant-volume soil sampler was used to obtain undisturbed samples for this determination. This sampler contained a waxed cardboard cylinder (3 in. diameter, 3·5 in. deep) which when filled

could be slipped out easily and fitted with two tin lids to retain the undisturbed soil core.

In the laboratory, the air-dried soil was mixed gently on a rubber mat, the larger aggregates being carefully broken up, and the whole cone-sampled to obtain a sample of approximately 30 g. This subsample was weighed to 30 g., placed on a filter-paper, and brought to capillary saturation by moistening from below. After this treatment the soil was gently washed on to a nest of three graded sieves contained in a cylinder fitted with an automatic siphon as in the method of Downes and Leeper (1940). The sieving cylinder was filled with water from a cistern with a ball and float to ensure a constant head of water. Twelve sieving cycles (filling and emptying) of 2·5 min. each were required so that each sample was sieved for 30 min.

After sieving the contents of each sieve were washed into one evaporating basin, dried at 105° C., and weighed to obtain the weight of aggregated material in the sample $> 0{\cdot}25$ mm. diameter. The difference between this weight and the oven-dry weight of the soil sample was the weight of material $< 0{\cdot}25$ mm. in the soil that had not been aggregated. Downes and Leeper have called this the 'dust' fraction.

The material in the evaporating basin was dispersed after treatment with 6 per cent. hydrogen peroxide and normal sodium hexametaphosphate. Coarse sand ($> 0{\cdot}25$ mm.) was then determined.

The percentage disaggregation is then expressed as.

$$\frac{\text{per cent. 'dust'} \times 100}{100 - \text{per cent. coarse sand}}. \qquad (1)$$

If the coarse sand was not accounted for in the above equation, coarse-textured soils would appear more aggregated than they were.

(*d*) *Organic carbon*

Organic carbon was determined on each of the samples used for aggregate analysis by the rapid-titration method of Walkley (1935).

(*e*) *Porosity measurements*

The soil samples for porosity measurements were collected by hammering cadmium-plated steel tubes (2 in. diameter, 3·5 in. deep) into the soil. The effect of the percussion was lessened by placing a block of wood over the tube. After removal from the ground the soil was kept in the tube by a piece of organdie affixed to each end by rubber bands.

In the laboratory the tubes were saturated with water in a slowly filling container. The final level of the water in which they were immersed was just below the top of the steel tube. After allowing to stand at saturation overnight, the cores were placed on a Leamer and Shaw (1941) tension table. This enabled the cores to be subjected to tensions between 0 and 60 cm. water. The table used differed from the one used by Leamer and Shaw in that a 20-in. square, 0·5-in. thick plate-glass base was used to support the gauze and filter-papers. This enabled inspection of the base from below for the purpose of detecting air bubbles between the gauze

and surface of the table. The soil cores remained on the table for 30 hours.

Tension-moisture curves (data not shown) were constructed for each of the two soil types. The tensions at the point of inflexion of these curves were 27·6 cm. for the non-calcic red-brown soil at Chapman, and 27·8 cm. for the Wongan Hills sandplain soil. It is considered that these tensions are not unduly low. The slope of the curves indicated that the distribution of the pores in any size class is so very even that it is probably inappropriate to attempt any division of the pores into two groups—non-capillary and capillary. Russell (1949) has made the division between these two groups at 50 cm. tension of water. A tension of 40 cm. has been used by McHenry, Zook, and Rhoades (1950). Baver (1940) has developed a less arbitrary division on the basis that the pF at the flex point of a pF-soil moisture curve is the pF of the tension at which non-capillary pores are drained. This conclusion is based on the finding that the amount of water withdrawn from zero tension to that of the flex point is closely associated with the rate of movement of water through the soil column.

Non-capillary porosity was determined in soil cores equilibrated to 0-cm. of water tension. The core after saturation would be the more correct basis, but as the saturated soil cores lost considerable amounts of water after removal from the saturating container no definite weight could be obtained. Consequently, as 0-cm. tension was taken as the base the values for non-capillary pore space are actually lower than the true values.

After weighing at 0 cm. the cores were transferred to a second tension table at a tension equivalent to that of the flex point of the pF-moisture per cent. curve for the particular soil for 30 hours. The difference between this weight and the weight at 0 cm. was taken as the weight of water lost from the non-capillary pores. The results are expressed on a volume basis as the percentage of non-capillary pore space.

Capillary porosity was then determined by drying the core at 105° C. and weighing. The weight of water lost was expressed on a volume basis as the percentage capillary pore space.

(*f*) *The penetrometer*

A penetrometer identical to that used by Stone and Williams (1939) was used as a means of measuring soil structure. The instrument is manually dropped and readily portable. It is possible for two persons to take and record up to 300 readings in 30 min. with the instrument over an area of 2 acres.

The simplicity of this instrument and the rapidity with which readings can be made make it an ideal piece of equipment for inclusion in any investigation of soil structure.

Results

Each particular aspect of structure will be discussed separately with particular reference to the wheat treatments as this is the only one common to all four rotations. The detailed statistical analyses have been

presented elsewhere by Newton (1955). The analytical data for Chapman are presented in Table 2, and those for Wongan Hills in Table 3.

TABLE 2

Chapman. Soil Physical Data, 1954

Rotation	% *Disaggregation*	% *Organic carbon*	% *Non-capillary pore space repl.*		% *Capillary pore space repl.*		% *Total pore space repl.*		*Depth of penetration (0·25 repl. in.)**	
			(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
CW	548	6·21	130·3	153·9	198·1	196·3	328·4	350·2	260	247
F	763	2·98	177·1	172·8	140·6	151·9	317·7	324·7	327	306
W	753	3·60	122·5	113·9	177·3	191·5	299·8	295·4	267	238
F	610	4·35	203·3	184·3	141·9	151·9	345·2	336·2	333	325
W	594	4·13	138·4	112·7	178·1	193·7	316·5	306·4	236	230
P	619	4·65	67·5	40·0	209·9	220·6	277·4	260·6	100	100
F	619	6·74	77·7	155·0	207·8	178·3	285·5	328·3	189	276
W	592	6·20	120·1	103·3	197·0	208·9	285·0	275·0	213	199
L_1	532	7·59	60·3	51·6	224·7	223·4	285·0	275·0	112	113
L_2	535	7·15	59·0	50·4	224·2	223·4	283·2	281·0	93	96
Least significant difference:										
5%	65		0·389		22·5		11·73		16·2	20
1%	86		0·514		29·7		15·49		21·3	26
0·1%	100		0·662		38·3		19·93		27·4	33

N.B. Where the statistical analysis has shown no interaction between blocks and treatments, the treatment totals for each block are summed as one value, in which case the treatment totals represent the sum of 16 observations.

* Sum of 12 observations.

(*a*) *Disaggregation*

There is a general trend for disaggregation to decrease from the two-course to the four-course rotation. One of the surprising findings is the relatively low disaggregation in the continuous-wheat plots; at both localities this treatment is not statistically different from the wheat plot of the fallow–wheat–2 years lupins rotation.

These results would appear to contradict the orthodox concept that only during a ley period is aggregation built up, for aggregation has been maintained at a comparatively high level under continuous wheat. Drover (1956) has shown that the organic-carbon level of the continuous-wheat plots is almost equal to the levels of the four-course rotation, and these two are considerably higher than those of the other two rotations, particularly at Chapman.

The differences between two-, three- and four-course rotations, however, support the merit of inclusion of a ley period as a means of building up structure. In substantiation of these findings the fallow plots of the two-course rotation at Chapman are significantly higher (0·1 per cent. level) in disaggregation than the three- and four-course fallows.

(*b*) *Organic carbon*

Organic carbon was determined on each sample taken for the aggregation studies.

TABLE 3

Wongan Hills. Soil Physical Data, 1954

Rotation	% Dis-aggregation repl.	% Organic carbon repl.	% Non-capillary pore space repl.		% Capillary pore space repl.	% Total pore space repl.		Depth of penetration (0·25 in.)* repl.	
	(1+2)	(1+2)	(1)	(2)	(1+2)	(1)	(2)	(1)	(2)
CW	324	3·08	140·2	170·7	368·5	337·8	341·6	269	280
W_{53}, F_{54}	366	2·22	100·5	180·3	350·7	296·7	334·8	227	246
F_{53}, W_{54}	365	1·93	149·5	174·3	341·2	337·5	327·2	259	310
P_{53}, F_{54}	359	2·90	65·0	121·4	426·2	300·7	311·9	96	139
F_{53}, W_{54}	363	2·92	145·2	166·6	363·9	341·7	334·0	298	281
W_{53}, P_{54}	365	2·89	105·9	153·1	363·3	309·5	323·7	177	216
L_{53}, F_{54}	330	3·98	65·6	99·5	438·4	292·1	311·4	89	119
F_{53}, W_{54}	320	3·66	171·8	189·1	344·8	360·2	345·5	295	305
W_{53}, L_{154}	299	3·85	114·4	167·3	371·2	360·2	345·5	185	248
L_{153}, L_{254}	314	4·82	76·2	114·7	431·4	312·2	310·1	128	140
Least significant difference:									
5%	41	0·325	24·4		19·6	14·2		25	
1%	54	0·429	32·3		25·9	18·7		33	
0·1%	70	0·552	41·5		33·3	24·1		42	

N.B. Previous rotation treatment is given as the fallowing and sowing of lupins had not been carried out at the time of sampling.

Where the statistical analysis has shown no interaction between blocks and treatments, the treatment totals for each block are summed as one value, in which case the treatment totals represent the sum of 16 observations.

* Sum of 14 observations.

A highly significant (0·1 per cent.) negative correlation was found between organic carbon and percentage disaggregation. Other workers, including Browning and Milam (1941) and McHenry and Newall (1947), have reported similar correlations. It must be stressed that this correlation occurred despite the fact that the organic-carbon status of both localities is low by other Australian standards. Nevertheless it clearly indicates that organic carbon is a factor affecting the aggregation of the soil particles.

(*c*) *Porosity measurements*

Three measurements of the porosity of the soils were obtained, namely:

(i) Percentage non-capillary pore space;
(ii) Percentage capillary pore space;
(iii) Percentage total pore space (sum of (i) and (ii)).

Concerning the non-capillary porosity at Chapman, there were no significant differences between any of the rotations. On the other hand, in all rotations the decrease in non-capillary porosity is in the order fallow > wheat > pasture, and these differences are significant (0·1 per cent. level).

At Wongan Hills there are no such trends due to the failure to carry out fallowing and seeding of the respective treatments at the normal time.

At Chapman the percentage capillary porosity of the four-course wheat

plots is significantly higher (5 per cent. level) than the respective two- and three-course plots. The capillary porosity of the four-course fallow is significantly higher (0·1 per cent. level) than the two- and three-course fallow treatment.

The decrease in capillary porosity is in the order of pasture > wheat > fallow. These decreases are in most cases statistically significant at least at the 5 per cent. level. There are no general trends evident at Wongan Hills, due to the failure to carry out fallowing and seeding.

In general the data for the percentage total porosity in the soil are so closely related to those for percentage non-capillary porosity that it is apparent that this latter factor is the one which has the greater effect on total porosity. It will be remembered that total porosity was obtained from the sum of the non-capillary and capillary porosities.

The data for total porosity, however, are generally inconclusive, as were the other porosity data. In all cases the total porosity is in the order of fallow > wheat > pasture for any of the rotations.

(*e*) *Penetrometer results*

There are considerable variations in both direction and significance in the data for the wheat plots at both localities. At Chapman the fallow in the four-course rotation has a significantly lower (0·1 per cent.) result than the fallow treatments in the two- and three-course rotations.

For any given rotation the decrease in depth of penetration of the probe is in the order of fallow > wheat > pasture. In most cases these results are highly significant.

Discussion

Table 4 shows the significance of the regression analyses for several pairs of structural measurements.

These indicate that organic carbon and aggregation are significantly correlated. Non-capillary porosity is correlated with total porosity and with penetrometer readings. It may be argued that non-capillary porosity is correlated with total porosity since the former is a part of the latter. Consequently, certain partial correlations were made to see whether non-capillary porosity or total porosity, or even both, affected the penetrometer readings. The results in Table 4 clearly show that it is the non-capillary porosity alone and not total porosity which is correlated with the penetrometer.

From the results presented it is possible to postulate certain factors which induce and vary aggregation in these two coarse-textured soils. As their clay content was small it is necessary to consider other cementing agents for the primary particles. At both localities, organic carbon was negatively correlated with disaggregation, which more than suggests that organic-matter content of the soils is making an important contribution to the formation and stability of aggregates. Other substances, however, such as iron and aluminium compounds, may be important, particularly in the lateritic soil from Wongan Hills. Compaction of the soil by root growth is likely to be important since the disaggregation decreased from

TABLE 4

Significance of Regression Analyses

Regression of†	*Regression sign*	*r*	*Chapman significance*‡	*r*	*Wongan Hills significance*
r56	−	0·736253	***	0·764156	***
r15	−	0·535205	*	..	n.s.
r25	+	0·705638	***	0·704532	***
r12	−	0·939659	***	0·930305	***
r13	+	0·917382	***	0·854591	***
r23	−	0·729261	***	..	n.s.
r14	+	0·965580	***	0·888556	***
r24	−	0·933297	***	0·770583	***
r34	+	0·850000	***	0·837925	***
Partial correlations were made on non-capillary porosity, total porosity, and penetrometer readings; the data are shown below:					
r14·3	+	0·886207	***	0·608526	**
r34·1	−	0·345868	n.s.	0·329808	n.s.

† 1. Non-capillary porosity;
2. Capillary porosity;
3. Total porosity;
4. Penetrometer;
5. Organic carbon;
6. Disaggregation.

‡ n.s. not significant;
* 5% level of significance;
** 1% level of significance;
*** 0·1% level of significance.

fallow to pasture to wheat, as did also the non-capillary porosity. This finding and the presence of a thin surface crust on some of the soils also suggest that cultivation and raindrop action are two of the main factors affecting the destruction of the weakly cohesive aggregates.

No conclusive results were obtained from the aggregation data from Wongan Hills. This was influenced by two factors. Firstly, the fallow and pasture treatments had not been prepared and, secondly, the proportion of coarse sand was not constant but steadily increased from the first plot to the twentieth. Downes and Leeper (1940) have drawn attention to the limitations of the method (Equation 1) on soils of variable mechanical composition. A randomized block design would have been more suitable as this design overcomes variations in the mechanical composition of the soil.

As a general tendency the highest values for aggregation, organic carbon, and capillary porosity occurred in the continuous-wheat rotation and the four-course rotation which included 2 years of legumes. In contrast, the non-capillary porosity, total porosity, and penetrometer measurements show virtually no significant differences between the results for any treatments in each rotation. Within any one rotation the values for aggregation, organic carbon, or capillary porosity decrease in the order pasture > fallow > wheat. The values for non-capillary porosity, total porosity, and penetrometer readings decrease in the order of fallow > wheat > pasture. Since fallowing destroys the aggregates the elimination of this cultural operation from the rotation would help to

preserve aggregates and maintain a favourable condition of porosity which could be obtained by cultivation prior to cropping.

At Chapman in particular, soil carbon and nitrogen values have declined seriously as a result of fallow–wheat and fallow–wheat–pasture rotations (Drover, 1956) which have continued for 24 years. These findings are supported by decreases in the stability of the soil aggregates to a wet sieving technique that are reported as disaggregation values.

The lateritic sandplain soils from Wongan Hills, used in this study, are usually regarded as having a single-grain structure. This is clearly incorrect. The results presented here not only demonstrate that some aggregation occurs but indicate some of the factors which influence it.

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A FIELD METHOD OF MEASURING SOIL/METAL FRICTION

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Summary

A method is described for measuring the mean value of soil/implement friction over a given depth in the field. The results of experiments using this technique indicate that the simple laws of friction are applicable to soil/metal interfaces, provided that allowance is made for the existence of an adhesive component which is independent of the applied normal load.

Introduction

It has been suggested that the bulk of the energy absorbed in tillage is used in soil/implement friction, the compression of soil, and the lifting and shearing of soil (Payne and Fountaine, 1952). Subsequent work has confirmed the importance of three of these, but has shown that compression need only be measured where the disturbances are small enough not to fail the soil; that is of the order of $\frac{1}{2}$ in. (Payne, 1955). In order to calculate the work done in lifting a piece of soil, its volume and density must be known. Standard techniques for measuring density are given in *Soils, Concrete, and Bituminous Materials* (1943), and the volume disturbed is a function of the shear strength of the soil and its frictional properties (Payne, 1955). The torsion shear box (Payne and Fountaine, 1952) has proved to be a satisfactory method for measuring the strength of topsoils. It is in regular use for research and tractor testing at the N.I.A.E. and has been adopted as a standard measurement for the latter purpose by a number of other European countries. It is with the measurement of the remaining property—soil/implement friction—that this paper is concerned.

Measuring Technique

Soil/implement friction (generally soil/metal) is defined in this work as the tangential force produced at the interface when soil slides over another material. Only those variables necessary in evaluating this force under practical conditions and for a given pair of surfaces are considered. Changes in other variables such as moisture content are regarded as changes in quality of one of the surfaces.

In previous investigations (Haines, 1925; Nichols, 1925, 1932; Wells, 1950) the normal load has been applied as a dead weight. This has the advantage that its value is under complete control, but it necessitates working on an artificially prepared horizontal surface which must be somewhat different in properties from that met by a cultivation

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implement. Moreover, where the apparatus sinks into the ground the force measured must contain a component contributed by the wave of soil pushed before the apparatus. This may introduce an unwanted variable —the bearing capacity of the soil. An attempt to overcome these difficulties has been made by arranging the apparatus so that the soil/metal interface lies in the vertical plane and by excluding from the measurements the force on the leading edge of the slider. Hence the average friction over any depth up to the limit for the apparatus (8 in.) can be measured. The apparatus, which is described in more detail by Rogers and Tanner (1955) and illustrated in Plate 1, Fig. 1, consists of a wedge-shaped vertical tine (apex leading) suspended on the toolbar of a tractor. The whole of one side of the tine, except a narrow strip at the leading edge, forms a sensitive plate on which the forces in two mutually perpendicular directions are measured. The characteristics of strain gauges enable these forces to be recorded with very small deflections of the sensitive plate and from these measurements the normal and tangential components on the interface are known. The value of the normal load can be altered from slightly above zero to the maximum by rotating the whole tine about its vertical axis, and is very sensitive to small changes in this setting. Its maximum value is, of course, limited for any particular soil, but must cover that range which could be met in practice by cultivation implements. The direction of relative movement between the soil and the slider may not be absolutely horizontal. To allow for this the sensitive plate is painted with engineers' marking fluid before being used and the average inclination of the scratches made by the soil is noted. If this is more than 10°, a correction is applied to the results according to the formula

$$\tan\delta = \frac{\tan\delta'}{\cos\beta},$$

$$\text{where } \tan\delta = \frac{\text{true tangential force}}{\text{normal force}},$$

$$\tan\delta' = \frac{\text{horizontal component of tangential force}}{\text{normal force}},$$

$$\beta = \text{inclination of scratches.}$$

In the experiments which have been carried out the inclination of the scratches has never been greater than 20°, which involves a correction of only 6 per cent. to the tangential force.

Experiments

The experiments with the apparatus on the first three soils were planned to find the relationship between normal and frictional loads at a range of speeds covering those commonly used in cultivation. The land was previously cultivated at right angles to the direction of the experimental runs. The treatment consisted of four nominal speeds arranged in four random blocks and the true speed of each run was measured by timing the tractor between marking posts. For the lowest speed the tractor-mounted friction apparatus was towed by a winch, but for the

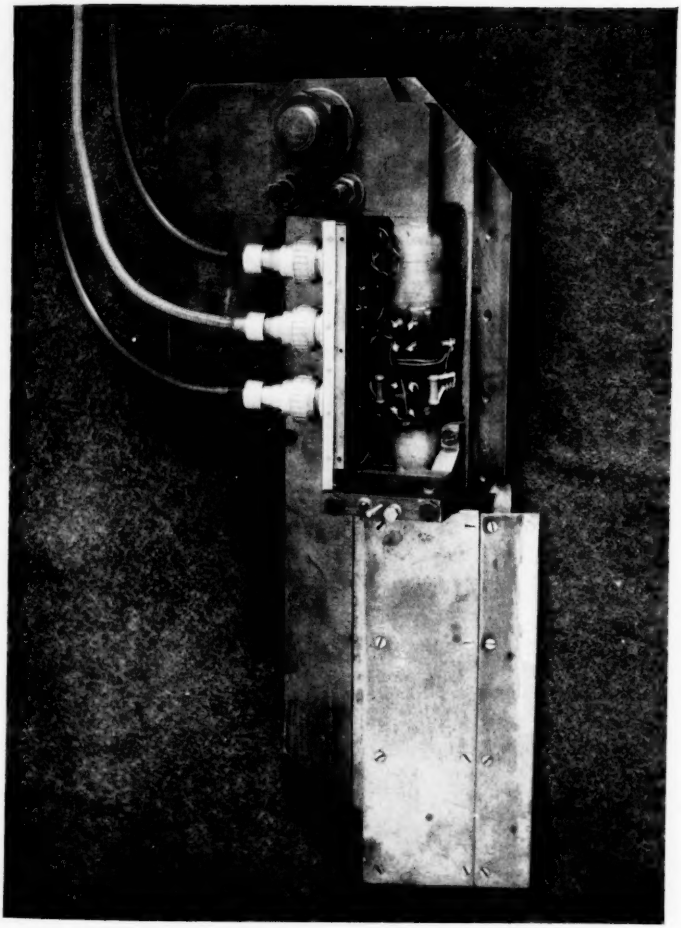

FIG. 1

P. C. J. PAYNE

higher speeds the tractor was self-propelled. It was found in these experiments that the normal load varied sufficiently with speed for it to be unnecessary to alter the setting of the tine about its vertical axis. The mean values of the normal and tangential forces, as found by a mechanical integrator (Rogers and Jevons, 1954), are plotted in Fig. 2. These curves show that the relationship between normal and tangential force was linear and independent of speed. The tangential force on sandy loam II has, however, a component which is independent of the normal load; in this case negative. The nature of this component is discussed later.

The experiments on the subsequent four soils were planned to discover whether this linear relationship with a component which is independent of normal load is characteristic of soil/metal friction phenomena and whether therefore a formula of the form $y = mx+c$, such as is assumed by civil engineers to hold for the shear strength of soil and for friction with masonry (Terzaghi, 1942), might also be used for soil/implement friction. The layout was exactly as in the previous experiments except that the difference between treatments consisted of changes in the angle of the tine relative to its forward movement. The forward speed was kept constant at about 1 m.p.h. by towing the tractor with a winch. The results are plotted in Fig. 3 and again show a linear relationship. The component which is independent of normal load is non-existent or negligible on three of the soils, but is quite clear on clay loam III.

Discussion of Results

The results indicate that the frictional properties of soil, at least over the range of moisture content at which cultivation can be carried out, may be represented by equation (1), similar to that for shear strength.

$$S' = C_a+\sigma \tan \delta, \qquad (1)$$

where S' = maximum tangential stress at interface,

C_a = tangential adhesion,

σ = externally applied normal stress on interface,

δ = angle of soil/metal friction.

It has been found in laboratory work (Payne and Fountaine, 1954) that the normal adhesion between soil and another surface is able to mobilize friction in exactly the same way as an externally applied normal load. Moreover, Fountaine (1954) found that the normal adhesion is the result of the moisture tension at the interface and can be shown to be numerically equal to it by allowing sufficient time for the tension at the interface to come to equilibrium with that in the rest of the soil and provided that there is sufficient water present to form a continuous film. Hence equation (1) can be written

$$S' = (t+\sigma)\tan \delta, \qquad (2)$$

where t is the average value of the moisture tension acting over the area of contact.

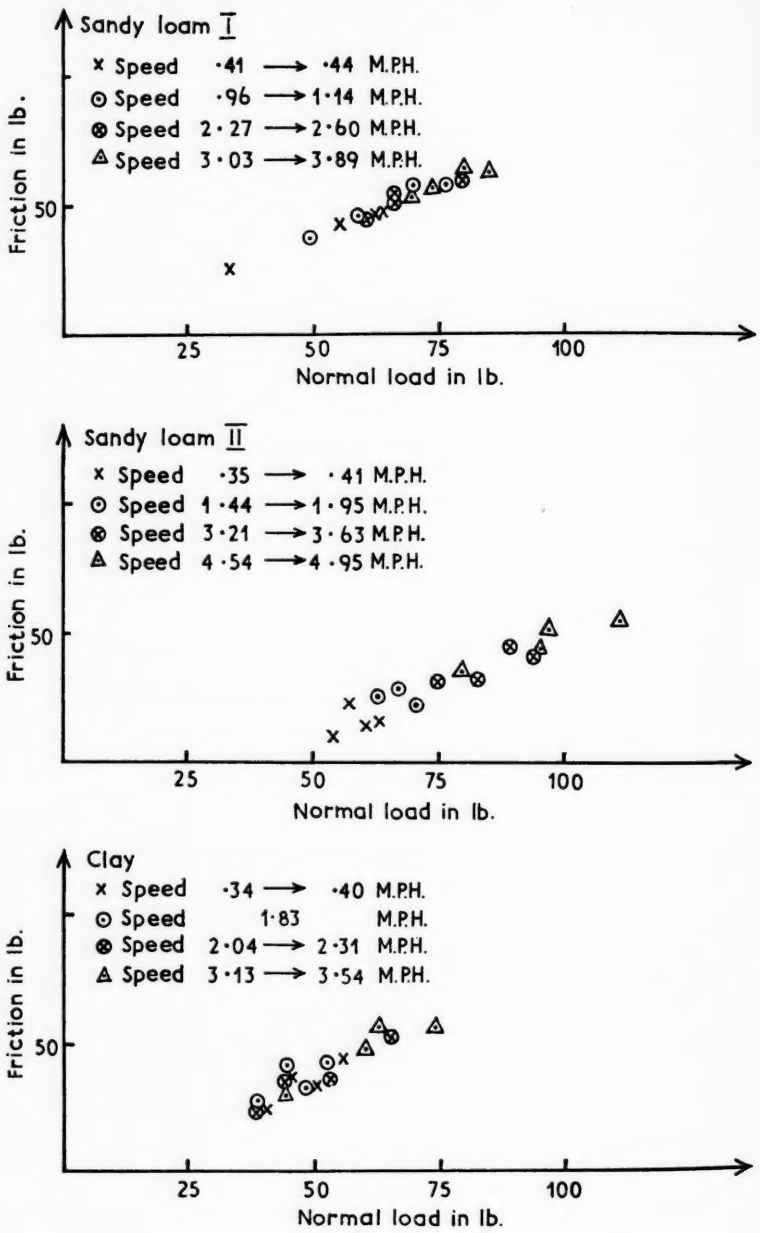
Sandy loam I
× Speed ·41 → ·44 M.P.H.
⊙ Speed ·96 → 1·14 M.P.H.
⊗ Speed 2·27 → 2·60 M.P.H.
△ Speed 3·03 → 3·89 M.P.H.
Friction in lb.
50
25
50
75
100
Normal load in lb.
Sandy loam II
× Speed ·35 → ·41 M.P.H.
⊙ Speed 1·44 → 1·95 M.P.H.
⊗ Speed 3·21 → 3·63 M.P.H.
△ Speed 4·54 → 4·95 M.P.H.
Friction in lb.
50
25
50
75
100
Normal load in lb.
Clay
× Speed ·34 → ·40 M.P.H.
⊙ Speed 1·83 M.P.H.
⊗ Speed 2·04 → 2·31 M.P.H.
△ Speed 3·13 → 3·54 M.P.H.
Friction in lb.
50
25
50
75
100
Normal load in lb.

FIG. 2.

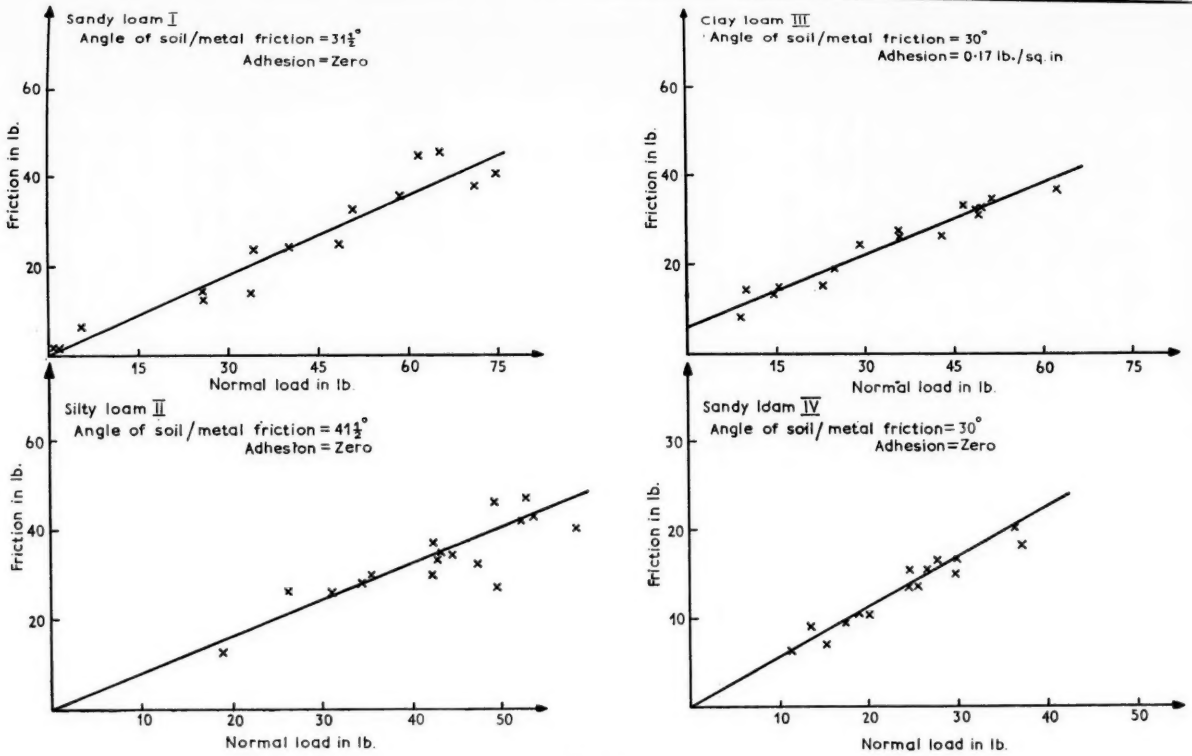
Sandy loam I
Angle of soil/metal friction = 31½°
Adhesion = Zero
Friction in lb.
Normal load in lb.
Silty loam II
Angle of soil/metal friction = 41½°
Adhesion = Zero
Friction in lb.
Normal load in lb.
Clay loam III
Angle of soil/metal friction = 30°
Adhesion = 0·17 lb./sq. in
Friction in lb.
Normal load in lb.
Sandy loam IV
Angle of soil/metal friction = 30°
Adhesion = Zero
Friction in lb.
Normal load in lb.

FIG. 3.

The form given in equation (1) is of more practical use than that in equation (2) since it is extremely difficult to measure the average moisture tension.

For the value of moisture tension at which the present experiments were carried out the low adhesion recorded would be expected. Even when the tension is high the adhesion may not be high, either because of discontinuity in the moisture film or failure of the tension to build up at the interface during the short period of contact. A possible explanation of the apparent negative adhesion on sandy loam II is that, where the applied normal stress was relatively small, it was carried entirely by the pore water which built up a pressure in the vicinity of the tine ($\sigma = t$, equ. 2). Where, however, the applied normal load exceeded a critical value, the pore water drained sufficiently to permit the excess normal stress to be carried by the soil particles and so the tangential stress commenced its linear increase. Though normally free draining, this soil does suffer severely from 'capping' and 'smearing'. Measurements of the shear strength, the results of which are given for all seven experiments in the table, also showed a negative value for cohesion. The slightly higher values recorded for the angle of soil/metal friction than for the angle of shearing resistance were quite unexpected but have been confirmed consistently.

TABLE I

Soil	δ	C_a (*lb./sq. in.*)	ϕ	C (*lb./sq. in.*)	ϕ/δ
Sandy loam (puddled) .	39½°	0	31°	1·1	0·79
Sandy loam . . .	41½°	−2·5	36°	− 0·2	0·87
Clay	39°	0	34°	3·8	0·87
Sandy loam . . .	31½°	0	27°	3·6	0·86
Silty loam . . .	41°	0	26°	2·3	0·63
Clay loam . . .	30°	0·17	25°	3·1	0·84
Sandy loam . . .	30°	0	22½°	0·3	0·75
Mean . . .	36°	..	29°	..	0·81

Conclusions

The results suggest that the angle of soil/metal friction is independent of speed, but more data is needed before this can be assumed under all conditions. The effect of speed found by Nichols on soils of low bearing capacity may have been due to a wave of soil pushed in front of the slider.

As concluded by Nichols and Wells, a definite angle of soil/metal friction may be measured for any pair of surfaces. This angle is probably independent of the moisture content and area of contact, but, owing to the ability of the moisture tension at the interface to act as a normal load, the value of the tangential force can depend upon these two variables. This is best dealt with in practice by assuming friction to possess two components—one proportional to the applied normal load and the other proportional to the area of contact.

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THE ACID SOILS OF THE SAN DIEGO MESA, CALIFORNIA

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Introduction

THERE is an extensive sequence of coastal terraces in the San Diego district of Southern California. The most conspicuous terrace, the San Diego Mesa, is a physiographic unit. It is much dissected by differential erosion, but where best preserved forms a broad, relatively flat plain several miles wide. The occurrence of highly acid soils on this terrace under semi-arid climatic conditions with a mean annual rainfall of about 10 in. is of considerable pedological interest. Widely accepted generalizations about the relationships between soils and climates would not lead one to expect acid soils in such an environment. Where such soils occur in arid climates they have usually been interpreted as old soils, formerly subjected to differing and more humid climates, and Carter (1951) has already claimed that the San Diego acid soils must represent a former time of more humid climates. The present paper records the major results and implications of a field investigation into this pedological anomaly, and gives a simple explanation in terms of the soil-forming factors. It is also hoped that a fuller account can be presented later where subtleties of the local geology and geography can be more adequately expanded.

The Location and Characteristics of the Acid Soils

To all intents and purposes the highly acid soils belong to only two series as mapped in the soil surveys (Storie and Carpenter, 1929, 1930), the Redding and the Carlsbad series.

The Redding series on the San Diego Mesa is best developed where the Mesa is capped by a brownish, resistant sandstone and conglomerate known as the Sweitzer formation, of post mid-Pliocene age (Hertlein, 1929). A similar soil, also mapped as Redding, occurs on the adjacent Poway Mesa, which is some 300–400 ft. higher than the San Diego Mesa where they abut. Here the soils are developed from the Poway conglomerate of Eocene age (Ellis and Lee, 1919; Hanna, 1926). A limited amount of typical Redding soils occurs on the Avondale terrace, the terrace next lower than the San Diego Mesa. The parent material in this case resembles the Sweitzer formation. Where the San Diego Mesa is not covered by a veneer of Sweitzer, the soils do not belong to the Redding series.

The most widespread soil of the Redding series is the Redding gravelly sandy loam, which has been described (Storie and Carpenter, 1930) in the following terms: '. . . a 5 to1 4 inch surface soil consisting of bright brownish-red or light reddish-brown gravelly loam. The content of gravel varies, although in most places it comprises more than 25 per

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cent. of the soil mass. . . . The subsoil is red clay which is very compact. . . . It is underlain at a depth ranging from 14 to 30 inches by a hardpan-like substratum. . . .' The surface horizons are usually only slightly acid, but reaction values as low as pH 4·5–5·0 are frequent in the clay subsoil (Fig. 1 (1) and (2)).

The Carlsbad soils are only slightly acid. They occur on a sequence of old, wind-piled sand ridges. They are interesting soils because they have morphological features typical of laterites of the Buchanan type. Although less acid than the Redding gravelly sandy loam, the Carlsbad resembles it in becoming more acid with depth, and in being underlain, at depths usually between 24–36 in., by a hardpan-like ('sandstone') substratum. The solum above the hardpan is normally a greyish-brown, loamy fine sand, characterized by numerous ferruginous concretions. A yellowish, mottled, sandy clay loam or sandy clay is frequently present immediately above the hardpan. From the hardpan down, the deep 'subsoil' is often strikingly red with pale grey mottlings.

The San Diego Mesa is interpreted (Hertlein and Grant, 1944) as a plain of marine denudation cut into Eocene and Pliocene sediments during a retreat of the sea. The Sweitzer formation is a superficial deposit (6–20 ft. thick) spread over the marine-planed surface. It is significant that the extent of the typical Sweitzer formation is almost identical with that of the underlying marine-planed Poway conglomerate. The old dunes on which the Carlsbad series is formed are believed to mark periods of still-stands during the retreat of the sea off the Mesa—probably in upper Pliocene times. Lower terraces definitely established as Pleistocene occur on the seaward side of the San Diego Mesa, and also along some of the streams. As already mentioned, soil mapped as Redding occurs on one of these—the Avondale terrace.

The Redding Soils and the Soil-Forming Factors

On theoretical grounds, and from the wide general experience of pedologists, we might consider that it does not appear normal for soils with as high acidity as the Redding to occur in such an arid environment. Two explanations seem possibilities; either that there has been a considerably more humid climate in the past, or that the acidity is due primarily to the parent material. For want of a simpler hypothesis, it was decided to seek an explanation in terms of differing past climates, and the parent materials.

Climate and climate history

The relationship of the Sweitzer formation (post mid-Pliocene) to the lower terraces (definitely established as Pleistocene) suggests that the probable age of the San Diego Mesa surface is late Pliocene or early Pleistocene. Climatic fluctuations have been a feature of the climates of many regions from that period until the present. It has to be anticipated, therefore, that since its final emergence the San Diego Mesa surface has experienced some fluctuations in climates. However, these do not appear

to have been of great pedological significance, as the following reasoning will indicate.

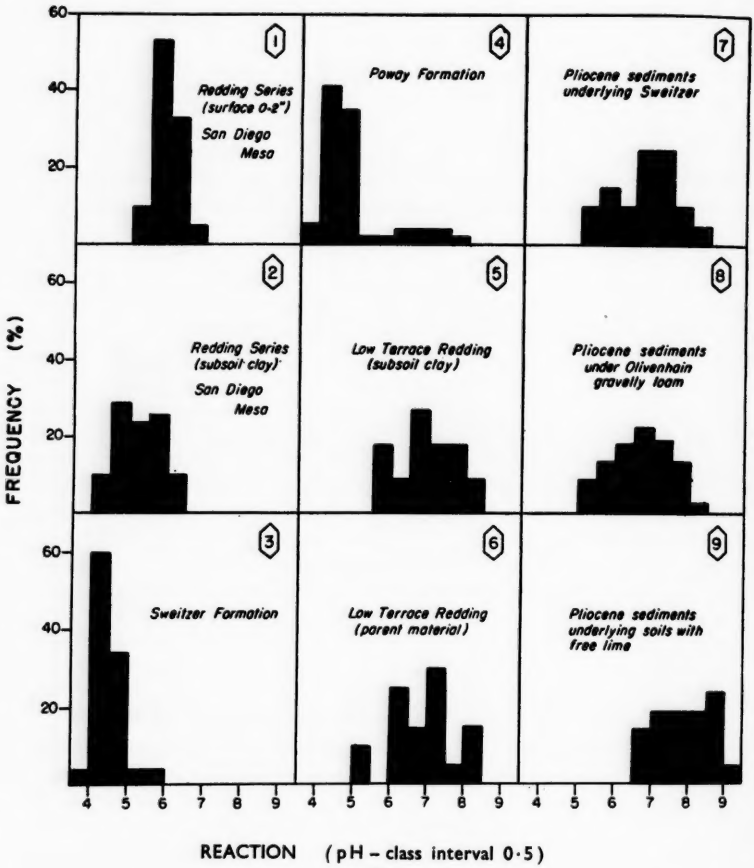

FIG. 1.

As the San Diego Mesa as a whole has the same general slope, and is a relatively small area parallel to and flanking the coast, with no pedologically significant current climatic gradient, it is to be expected that past climates, at any one time, would have been 'pedologically uniform' over the Mesa surface as a whole. Thus all preserved surfaces of the Mesa should have experienced an identical climatic history. If this included humid periods intensive enough to produce soils with as low reaction as the Redding gravelly sandy loam, then we might expect that evidence of this humidity would also be observable over the Mesa surface as a whole. No such evidence is apparent, and the Mesa soils range from the highly acid Redding to the chernozem-like Altamont and Diablo series.

Much the same argument can be applied to the Carlsbad series, which is of equivalent pedological age to the Redding.

The parent material factor

The Sweitzer series, as defined by Hertlein and Grant (1944), is co-extensive with the Redding series on the San Diego Mesa. It is very nearly co-extensive with the marine-planed Poway conglomerate. The relationship is so close that it can hardly be considered accidental. It is indeed apparent, although the argument cannot be developed fully here, that the Sweitzer is a superficial deposit derived from the underlying, or adjacently underlying Poway conglomerate. Where other sediments were truncated, any superficial deposits on the San Diego Mesa have been more closely akin to them.

As the Sweitzer formation is the parent material of the acid Redding soils, its own reaction is of interest. Of fifty samples of Sweitzer formation taken at depths considered to have been insignificantly influenced by the soil-forming processes, all were acid, and 95 per cent. of them had reaction values of less than pH 5·0. The results are summarized in the frequency distribution diagram in Fig. 1 (3). It is apparent then that the acidity of the lower horizons of the Redding soils about San Diego is closely correlated with the acidity of the parent material—the Sweitzer.

The strong genetic link between soils developed on the Poway conglomerate and on the typical Sweitzer formation suggested by the fact that the Redding series occurred on both, and by the close lithological and geographical relationship of the two formations, is further strengthened by an analysis of the reaction of the Poway. The results of fifty samples taken in cuts over Highway 395 on the Poway Grade are summarized in the distribution diagram Fig. 1 (4). They showed a wider range of values than did the Sweitzer, but 80 per cent. of the samples had pH values of less than 5·0, and the lower strata, those which might have been reworked to give the Sweitzer veneer, were all highly acid.

Thus the occurrence of highly acid soils and acid parent materials are closely correlated.

The close relationship between the nature and reaction of the parent material and the soil reaction applies to other parent materials on the original surface of the San Diego Mesa (Fig. 1 (5) and (6), (8) and (9)). For example, where the parent materials are calcareous, as in the eastern Chula Vista Mesa and eastern Otay Mesa subsections, calcareous soils like the Linné and Ayar series occur.

Discussion

There appears no doubt at all that the character of the soils on the San Diego Mesa have been strongly influenced by the nature of the parent materials. As the surfaces are very old, this indicates that, at least under these conditions, the impress of parent material is not lightly eradicated.

The climatic factor is more difficult to assess. However, the close relationship between the parent materials and the soils makes it unnecessary to assume very large climatic changes to explain the acidity of the

Redding soils. The occurrence of contiguous soils ranging from highly acid to calcareous series on surfaces of equivalent age and relief strongly suggests in fact that there has been no major climatic shift. Indeed, excepting the Redding and Carlsbad series, the soils associated with the different parent materials do not appear to be very different from the types one would reasonably expect in the climate existing today, and the Redding and Carlsbad are understandable if one considers the character of the parent materials. Nevertheless, there are some pedological facts which are difficult to reconcile, at least spontaneously, with the low rainfall of the San Diego region. The most pertinent of these, the question of clay formation in the Redding series and the presence of the lateritic Carlsbad, will be briefly discussed.

Since the Redding series has a well-developed clay subsoil, its acidity is only partially explained by the acid parent material. As most of the clay probably formed *in situ*, it is necessary to explain the formation of the acid clay. It is suggested that during clay formation the amounts of calcium released have been exceedingly small, and have been continuously taken up by the vegetation and micro-organisms. Much of this calcium would later be returned to the soil as organic residues, probably mostly to the surface layers. This explanation conforms both with the fact that the surface horizons of the Redding soil are either neutral or slightly acid, and the subsoil clay highly acid, and with the exchange data for the typical Redding gravelly sandy loam. The surface inch contains from 3·5 to 6 times as much exchangeable calcium as the other parts of the profile. It does not seem essential, therefore, to invoke a drastically more humid climate to explain the acid days.

The morphological features of the Carlsbad series are usually considered associated with a much moister tropical climate, and the soils are strikingly similar to some of the 'laterite' soils in Australia which have been interpreted as indicative of a past warm humid climate. Yet this explanation does not necessarily hold here. It is known that the Carlsbad sands were originally acid (they were built up largely from Sweitzer-derived sands), that they were, and are, very high in iron-bearing minerals, particularly magnetite, and that since the hardpan developed they have been subjected to periodic restricted drainage. Rim (1951) has shown that magnetite-rich sands associated with dunes along the Israel coast, under a climatic régime not much more humid pedologically than San Diego, produce red soils through the hydrolysis of the iron-rich minerals, and that in mature soils on such parent materials the hydrated sesquioxides become concentrated near the surface as a result of transport in ascending solutions. The sands of the old beach ridges near San Diego appear to have been much higher in iron-bearing minerals than the Israel dunes. Taking these facts into consideration, along with the fact that no other soils of equivalent age in the region have similar, or even remotely similar features, the unexpected Carlsbad characteristics may perhaps also be mainly ascribed to the parent material. The climate during their formation, although at some stages more moist, may not have been radically different from today.

The conclusion seems reasonable then that, while it is likely that the

climate of the San Diego region has fluctuated since late Pliocene, and somewhat moister periods than the present have occurred, the evidence for such changes and their intensity must be sought in directions other than the soils. Such pedological evidence as exists does not suggest any greatly different climate. The acid Redding soils indicate that, in the absence of any ready outside source of metallic cations, acid soils can persist almost indefinitely on non-eroding and non-accumulating surfaces in arid environments.

Summary

A pedological inquiry has been made of the anomalous, highly acid soils which occur in the arid environment of the San Diego Mesa in Southern California. These soils have long been puzzling to soil scientists, but it has usually been considered that their acidity is a relic feature relating to a considerably more humid past climate. Pedological evidence is produced to support a line of *a priori* reasoning, which suggests that it is not necessary to invoke a radical change of climate to explain the presence of these highly acid soils, and that the nature of the parent material has been a more significant factor in their reaction. Acid soils in semi-arid environments cannot, in themselves, be considered as indicative of climatic change. Each particular case needs to be considered on its merits.

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AN INDURATED SOIL HORIZON FORMED BY PERMAFROST

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THE presence of a very compact or indurated layer in many freely drained Scottish soils has been recognized for many years. This horizon has been recorded by a number of workers in Scotland and elsewhere as occurring in a wide range of soil series and throughout a wide range of climate, topography, parent material, and vegetation.

Glentworth (1944) was the first in Scotland to attempt a detailed examination of this layer and to describe some of its physical and chemical characteristics. His findings were later confirmed and amplified by Glentworth and Dion (1949), FitzPatrick (1951), and Glentworth (1954).

Muir (1949) has commented on the occurrence of a rather platy-structured indurated horizon at the bottom of the B horizon in many soils in the north-west region of America. This horizon he considers similar to the indurated layer both from the chemical and physical aspects. He states that it has been called a 'fragipan' by American workers. According to Smith (see Glentworth, 1954, p. 136) the indurated layer in north-east Scotland is similar to the 'fragipan' horizon of certain grey-brown podzolic soils of the U.S.A.

During a visit to Norway in the summer of 1954 the author recognized in many different Norwegian soil series structures identical with those found in the indurated layer in Scotland and came to the conclusion that they must have been formed in a similar manner.

From the above it is clear that indurated layers with similar characteristics occur in various soil series and in widely separated parts of the humid-temperate region. There does not appear to be any contemporary common process operating to account for their formation, but in the past all the regions concerned were subjected to periglacial conditions. Observations described below suggest that the structural features present in these horizons were produced under perennially frozen conditions or permafrost.

In order to get a clear picture of the indurated layer and its relation to the profile morphology and environment, a list of the features exhibited by the layer and its environment will be given. Although this paper is meant to deal only with the macrostructure of the layer it is necessary to mention some other features which are known to exist and are considered to be significant. Many of these features although not directly associated with the indurated layer will nevertheless lend weight to the suggestion that the structural features have been inherited.

1. The indurated layer is found developed throughout a wide range of topography, parent material, and vegetation and under considerable variations in climate within the humid-temperate region (Glentworth, 1954).

2. It is always found in an area which is known or thought to have had a periglacial climate during and/or after the last glaciation.

3. It occurs in a large number of soil groups which include Brown Earths, Podzols, Peaty gley Podzols, Brown Podzolic Soils (Glentworth, 1954).

4. It occurs on flat or undulating ground and also on slopes as great as 35–40°, the land surface being usually smooth or gently undulating.

5. It usually occurs in freely drained soils where it may be very hard and resistant to penetration by spade or auger, although detached blocks are easily broken by hand. Under conditions of imperfect drainage the characteristic structure of the layer is usually retained, but without any induration.

6. It is usually found at a depth of 16–24 in. from the surface of the soil (Glentworth, 1954).

7. In any one given locality it occurs at a fairly constant depth, although its position in the profile may be deeper on the lower slopes in hilly regions (Glentworth, 1944).

8. It varies much in thickness. It may be only a few inches thick and occur as a B_3 horizon or it may extend from the B horizon to a great depth below the solum.

9. Its upper surface is sharply defined (Plate 1, Fig. 1) while the lower surface is usually diffuse (Glentworth, 1954).

10. It exhibits both a massive and a platy structure in the profile. The platy structure is best developed near the top of the layer (Plate 1, Fig. 2), while it is usually massive below. The massive blocks can usually be broken down into distinctly platy units.

11. It is somewhat impermeable to water under conditions of free drainage and in many places forms stream beds and the bottom of drains in forested areas (Glentworth, 1954).

12. It apparently arrests some of the processes of soil formation, for very often the B horizon of iron deposition stops abruptly over it, showing a tendency for a concentration of iron at the junction which sometimes takes the form of a thin iron pan.

13. There is usually a marked difference in colour between the indurated layer and the overlying horizons of the profile (Plate 1, Fig. 1).

14. It contains discontinuous spherical or vesicular pores or both (Glentworth, 1944).

15. The pore space is usually about 20 per cent. as compared with 50 per cent. for the horizons above and below (Glentworth and Dion, 1949).

16. Its texture is never very heavy, but considerable variations occur in different profiles and some variation may even be found within the layer itself.

17. The results of mechanical analyses show that the clay content of this layer is lower than that of the layer above or below it (Glentworth, 1944).

18. Around the larger separates ($>$ 2 mm.) there is usually a sheath of material finer in texture than the surrounding soil (Glentworth, 1944). This sheath is usually thickest at the top of the stone or boulder and usually absent beneath it

19. There is usually a marked absence of root penetration.

20. Chemical analysis of the clay fraction from this layer shows a relatively higher content of aluminium compared with that found in either of the adjacent layers (Glentworth, 1944).

It is necessary now to consider the method or methods of formation of the macrostructure exhibited by this horizon. Glentworth (1944) considers that the indurated layer 'is not an ortstein in that little or no visible iron accumulation is apparent, and it is thought that the induration occurs at the surface of the ground moraine upon which rested the glacial debris enmeshed in the decomposing ice-block at the close of the Ice Age. In the melting process water was probably passing over the ground moraine causing, through the water sorting process, the light textured B_2 horizon we find now.'

Muir (1949), on the other hand, considers that

> there really are two deposits separated by a pan layer; the lower till having been somewhat water-eroded and then frozen while the upper, looser material was laid down. A thin section of the hard pan from a soil on basic igneous till in Aberdeenshire shows very little cementing material on the whole, the coarser grains being jammed rather tightly together in many parts of the section with very few pores or crevices visible. A study of the hard pan in the Beltsville soils by Drs. Nikiforoff and Cady showed that its hardness could only be due to interlocking of the coarse particles since there was very little clay present. When the particles are pressed close together very little cement would be necessary to give induration (cf. Nikiforoff, Humbert, and Cady, 1948).

Now, if either of the above explanations were correct, the indurated layer should be found only in material deposited by glaciers, yet it has been observed in a variety of material deposited after the retreat of the glaciers. Also, it is extremely doubtful whether the material released from a melting glacier would form an even covering over the surface of its bed; whereas the loose material above the indurated layer is always of fairly constant thickness. Observations by the author in Spitsbergen show clearly that glaciers do not always leave smooth surfaces, but very often ragged ones while the nearby slopes which have been subjected to periglacial activity are very smooth and indeed similar to many Scottish slopes. Synge* and Galloway* have recently produced fresh evidence to show that there was a definite period of periglacial activity in Scotland since the laying down of the till which forms so much of the parent material of the soils.

It is here suggested that the indurated layer is the fossilized permafrost layer.

Taber (1943) has shown that in Alaska the permafrost has a structure of alternating plates of clear ice and frozen soil. He has reproduced this structure experimentally in the laboratory by gradually freezing a wet mass of soil from one direction. This caused a segregation of the wet mass into plates of clear ice and fairly dry frozen soil. The size of these units and the amount of segregation that takes place seem to depend on the amount of water present and also on the speed at which the material

* Private communications.

is frozen. When there is a large amount of water present and freezing is gradual a considerable amount of clear ice is formed, the soil forming lenticules in the ice. On the other hand, if freezing is rapid a massive structure is produced. Thus the structure which can be produced will vary from massive to definitely platy depending upon the speed at which it is frozen. It seems therefore that it is the process of gradual freezing under wet conditions which accounts for the presence of the platy structure in the indurated layer.

During the process of freezing, gases dissolved in the water will be set free in the freezing mass. As the freezing of the soil is taking place from the surface downwards, these gases will not be able to escape into the atmosphere and will therefore become trapped in the mass as it freezes. These gases will form separate small bubbles, the shape of which may remain spherical or become distorted to give a vesicular pattern. The production of this type of structure can best be observed by freezing ordinary tap water in a refrigerator. In a block of ice the air bubbles are usually spherical or cylindrical in shape, whereas in a block of soil they may be distorted into many shapes.

The influence of dissolved gases on the production of vesicular or spheroidal pores has been shown by freezing a mass of soil puddled (*a*) with ordinary tap water and (*b*) with ice-cold water saturated with carbon dioxide. In both cases pores are produced, but in the latter case the number and size of the pores are greatly increased.

Further tests were carried out to determine the effect of the presence of stones in a freezing mass of puddled soil. For this purpose a puddled mass of soil containing stones was frozen. The resulting block was then placed on a thick pad of filter-paper and allowed to thaw. When sufficiently dry, the block, which had maintained its shape, was broken open. It was then found that a coating of fine material had formed around each stone.

It has thus been shown that the three main features of the macrostructure of the indurated layer can be produced by freezing a wet mass of soil. These features are:

1. Platy structure.
2. Discontinuous spherical or vesicular pores.
3. Sheathing of fine material around the separates greater than 2 mm.

Since these structural features can be produced by freezing in the laboratory it seems reasonable to postulate that in the field they were produced under climatic conditions very different from those prevailing at present. Under contemporary climatic conditions in Scotland freezing does not extend to the depths at which the above phenomena are observed. In fact, as is known, freezing to such depths occurs only under periglacial conditions.

During the summer of 1954, the author, as a member of an expedition to Spitsbergen, was able to study soils existing under present-day periglacial conditions. Although the greater part of Spitsbergen is covered by ice there are a few areas where there is a good depth of soil very suitable for conducting investigations. The area chosen for study lies

immediately north of Longyearbyen, the capital of Spitsbergen. It is bounded to the south by Adventfjord and Advantdalen, to the east by Eskerdalen and Sassendalen, and to the north by Sassendalen and Sassenfjorden. The features of this natural geographic unit range from high hills and mountains to considerable stretches of flat or moderately sloping ground. About one-third of the total land surface is covered with ice and active glaciers. The greatest expanse of ice-free flat or sloping ground occurs in Advantdalen and it was in this valley that most of the soil investigations were carried out.

Examination of the permanently frozen subsoil in Advantdalen revealed all the features already described by Taber (1943). In particular, the laminar structure was present (Fig. 3). In addition the characteristic pores and the sheathing of stones and boulders with fine material were evident (Fig. 4).

In order to determine whether the material would maintain these structural features in the thawed condition, pits were dug to a considerable depth in the frozen soil and left open for a few days. On re-examining these profiles it was found that a considerable amount of thawing had taken place and the permafrost table had sunk by about 1 ft. This thawed material which, when the pit was dug, contained bands of clear ice, still exhibited all the macrostructural features described above as being associated with the indurated layer in Scottish soils.

In addition to the above experiment, blocks of frozen soil were removed and dried under four different sets of conditions:

1. on trays in direct sunlight,
2. on trays in the shade,
3. on thick pads of filter-paper in direct sunlight,
4. on thick pads of filter-paper in the shade.

The blocks which were placed on trays and dried in direct sunlight thawed out rapidly and formed a fluid mass which on drying became a solid mass of soil without the retention of any of the original structure. Those which were placed on trays and dried in the shade thawed more slowly than those placed in the sun, but they also became fluid masses and dried out as a solid soil mass. The blocks dried on filter-paper in both cases retained their original shape, but showed a marked shrinkage. The blocks dried on filter-paper in direct sunlight showed some loss of the structural features in the outside layers, while those dried on filter-paper in the shade retained the features throughout (Fig. 5), since the water set free from the gradually melting ice was quickly absorbed by the filter-paper. It was further observed that the disappearance of the ice encasing the stones had produced a void between them and the sheathing of fine material. It is presumed that this void when it exists in the soil would become filled with a further deposition of fine material carried down by percolating waters.

It seems evident, therefore, that the macrostructural features of the indurated layer are related to a permafrost condition, the upper surface of the layer representing the lower limit of summer thawing.

The process of structure formation in the indurated layer in Scotland

seems to have taken place in the following manner during the periglacial epoch which is presumed to have followed the last glaciation.

At first, summer thawing would take place to a considerable depth. Succeeding tundra conditions, with the accompanying vegetation and litter, would provide insulation which would cause a steady reduction in the depth of thawing. The reduction in depth of thawing would take place slowly, allowing the gradual but steady rise in the permafrost table. This gradual upward movement of the permafrost table would produce a marked development of alternating laminae of clear ice and soil which would account for the well-developed laminar structure of the indurated layer, especially at its upper surface. The presence of a continuous vegetative cover would also tend to cause the depth of thawing to be fairly uniform in any one given locality. This would account for the constant depth in the soil of the upper surface of the indurated layer. This effect of vegetation on the depth of summer thawing is clearly shown in Spitsbergen. Where there is no vegetative cover the permafrost is found at 3 to 4 ft. Where the vegetative cover is discontinuous, such as in areas of mud polygons, the permafrost is found nearer the surface in the presence of the vegetation and lower down in its absence. Where the vegetative cover is continuous, thawing takes place to a depth of 18 to 24 in., the upper surface of the permafrost being smooth or slightly undulating.

Further amelioration of the climate will result in the development of a dense vegetative cover as well as the melting of the permafrost, but under the protective action of the cover the melting will be gradual and the soil will therefore maintain its original structure.

Summary

The presence of a very compact or indurated layer in freely drained soils occurs in widely separated parts of the humid-temperate region. It is suggested that the structural features of this layer were produced under periglacial conditions. Evidence in support of this suggestion is provided by a study of the macrostructural and other physical features of the horizon together with the topographical conditions. The possible mechanism of the formation of the indurated layer is considered in relation to observations on permafrost in Spitsbergen.

Acknowledgements

I should like first to express my gratitude to Dr. R. Glentworth for introducing this problem to me. I should also like to express my sincere indebtedness to Dr. W. T. H. Williamson, whose stimulating interest made the completion of this work possible. My thanks go to Sir Thomas M. Taylor, Principal of the University of Aberdeen, whose interest made it possible for me to obtain a grant to defray the expenses of my visit to Spitsbergen.

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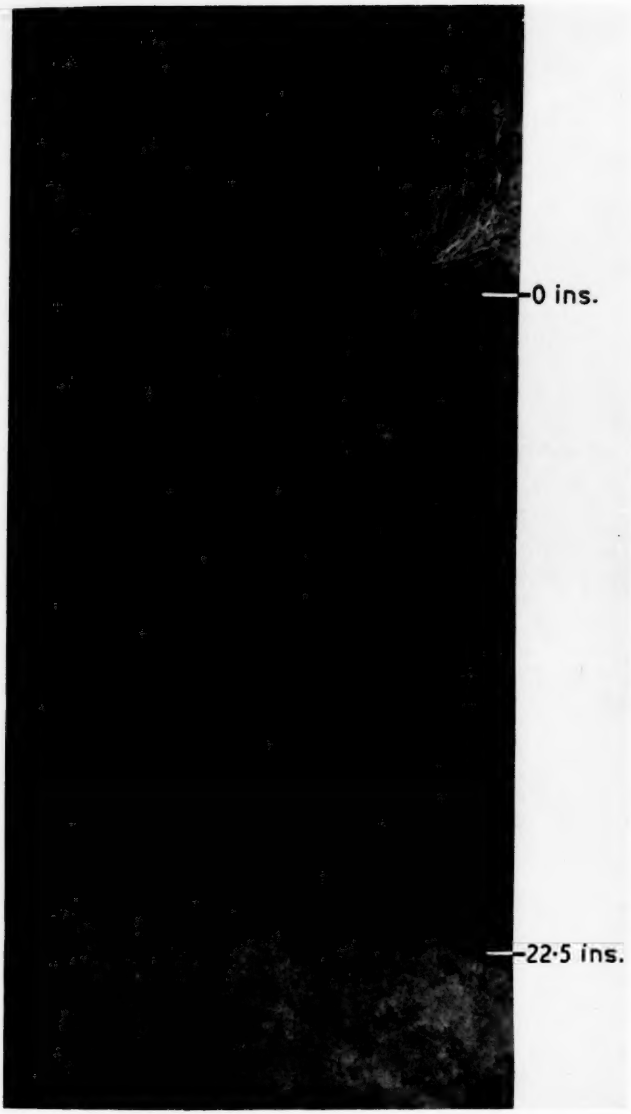

FIG. 1. A soil profile showing the sharp line of demarkation between the surface soil and the indurated layer. The marked difference in colour is also indicated

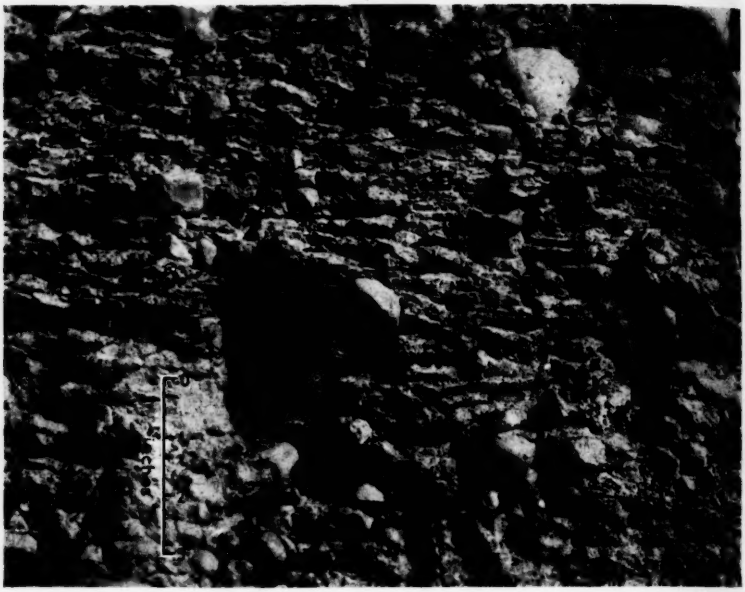

FIG. 2. Indurated layer showing marked development of the platy structure

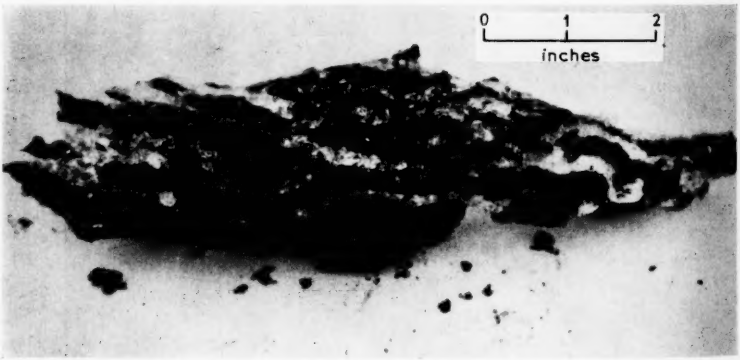

FIG. 3. A block of permafrost showing alternating laminae of clear ice and soil

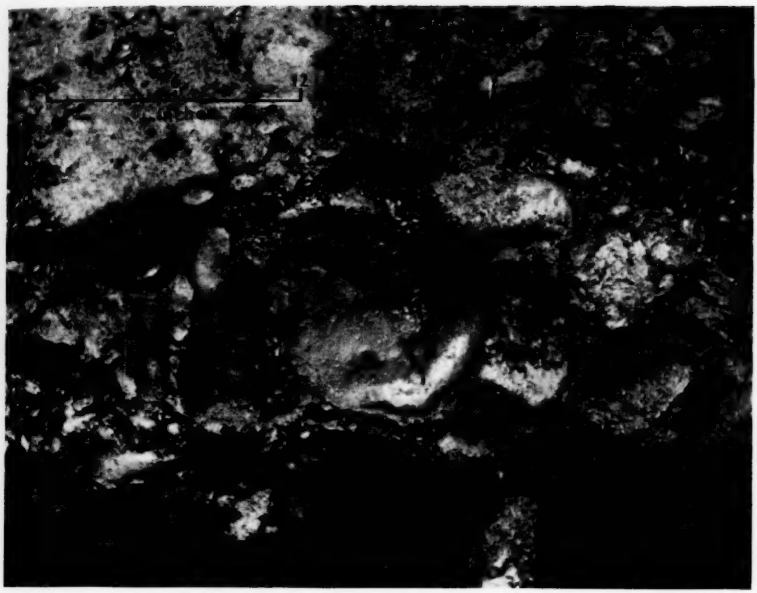

FIG. 4. An exposure of permafrost showing a casing of ice after large stones have been removed and also the sheath of fine material outside the casing of ice

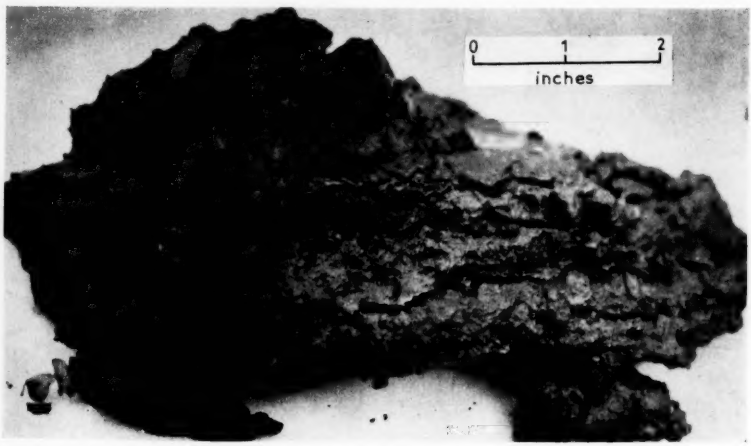

FIG. 5. A partially thawed block of permafrost showing a marked retention of the platy structure

E. A. FITZPATRICK—PLATE III

THE PALEOPEDOLOGY OF NORFOLK ISLAND

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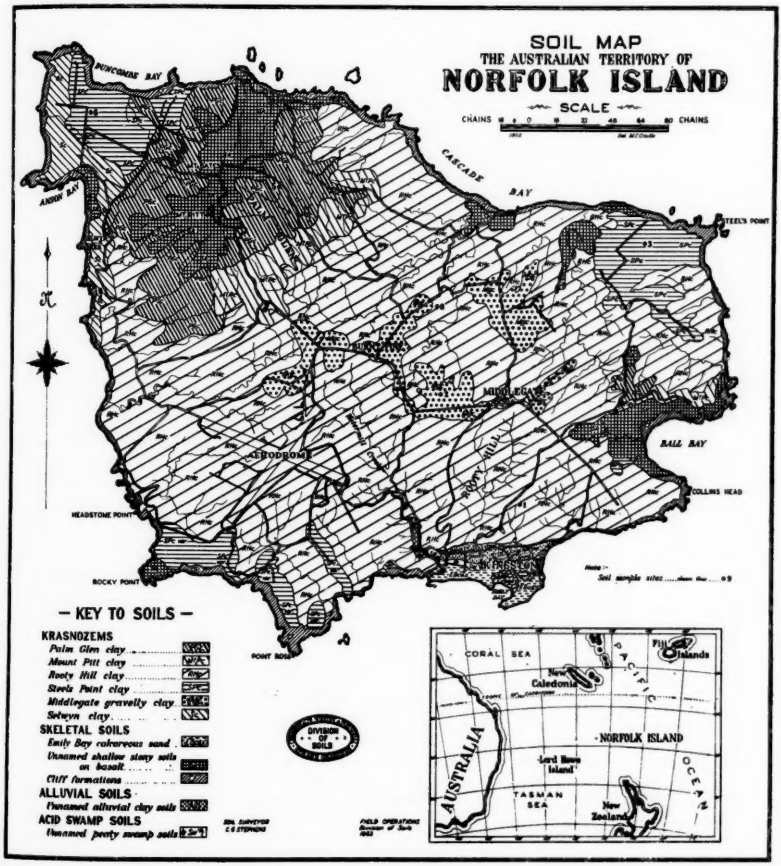
Introduction

In July 1953 a soil survey of Norfolk Island was made, primarily as a basis for the investigation of agricultural problems there. A Soils and



Land-Use Report by Stephens and Hutton (1954) has been issued. Certain morphologic, topographic, and fertility features of the soils noted by one of the authors (C. G. S.) during the course of the field work were interpreted as indicating a varied history of the soils and associated

physical features of the island. The laboratory examination of the soils by the other author (J. T. H.) revealed differences between soil types that could not be explained by the present-day terrain of the island and normal weathering of basalt. This paper co-ordinates the various observations to present the paleopedology of Norfolk Island soils.

The work of Marshall (1927, 1930) on the geological history of other volcanic islands in the South Pacific is used extensively in the interpretation of the geomorphic and petrological development of Norfolk and nearby Nepean and Phillip Islands.

Location and Size

Norfolk Island lies about 900 miles ENE. of Sydney on latitude 29° 3′ 45″ S. and longitude 167° 56′ 29″ E. It is a volcanic island about 8,500 acres in area and one of a group of three islands in this locality. Nepean Island, about half a mile to the south, is a limestone islet about 10 acres in extent, and Phillip Island, about 3 miles to the south, is a very rugged and precipitous volcanic island less than 2 miles long and narrower than 1 mile.

Present-Day Terrain

The three islands form a small and isolated group and are the only exposed land masses on the Norfolk Ridge, a submarine elevation described by Marshall (1910) and Brodie (1952) stretching from New Caledonia and its attendant islands to New Zealand. Both Norfolk and Phillip Islands are remnants of extinct volcanic cones, composed of interbedded layers of tuff and basalt flows (see Plate I (*a*)). Phillip Island, about 900 ft. high and generally steeply sloping and precipitous, is a mere fragment of a marine volcanic cone, only the northern portion of the rim being preserved. Norfolk Island, a larger remnant of a more extensive cone, is dominated by an abrupt fragment of its crater rim, which in Mt. Pitt and Mt. Bates rises to 1,044 and 1,028 ft. respectively. Ball Bay on the east coast of Norfolk Island is the remnant of a lower level parasitic cone breached by the sea.

Fig. 1 presents a reconstruction of the two cones of Norfolk Island. It is based on the present-day topography and drainage pattern of the island, the latter departing from the typical radial pattern where the major cone has been disrupted and planed off to the general height of the interior of the island, namely between 400 and 500 ft.

During the course of the field work, samples of basalt, tuff, and limestone were collected and have been examined mineralogically and chemically. The sample of basalt collected from Palm Glen is of normal character and chemically it is essentially similar to other basalts although less basic than many. The sample of tuff from Anson Bay consists mainly of nontronite, a clay mineral of the montmorillonite group probably formed by the action of water on the minerals normally present in volcanic ejecta. Chemical analysis shows the difference between it and basalt (Table 1).

The formation of clay minerals of the montmorillonite group when normal tuff is subjected to the action of water that is alkaline and con-

tains calcium and magnesium in solution has been discussed by Faust and Callaghan (1948), and it is most probable that this sample of tuff has been subjected to similar conditions.

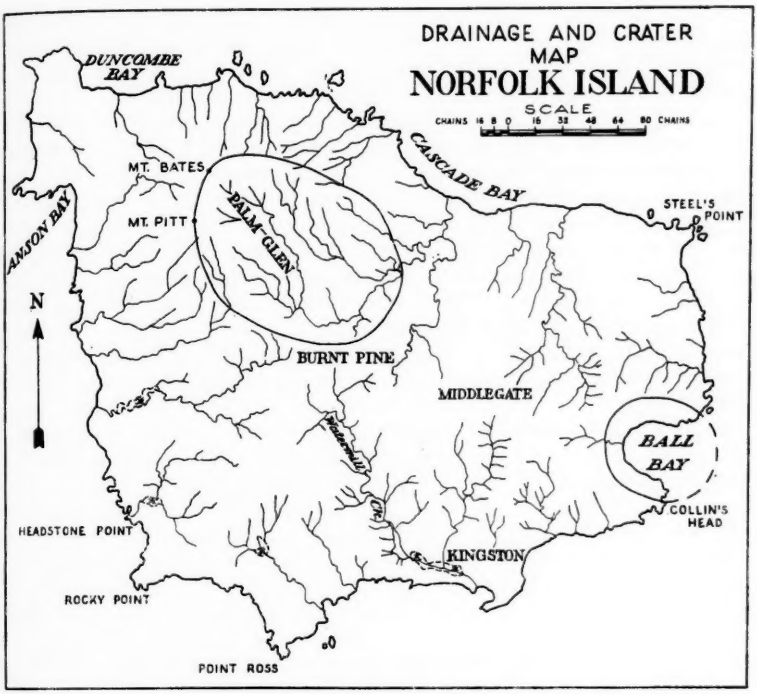


FIG. 1.

Except for a small sector at Kingston (see map and Plate II (*b*)) the island is ringed by cliffs which undulate up to 250 ft. above sea-level and on which there are remnants of benches and off which, on the north

TABLE I

Chemical Analysis of Basalt and Tuff

	Basalt	*Tuff*	*Basalts**
Si, % . . .	23	20	20
Al, % . . .	9	11	8
Fe, % . . .	7	7	11
Ti, % . . .	1	2	1
Ca and Mg, % . .	9	1	12
P (sol. in HCl), % .	0·11	0·008	..
Loss on ign., % . .	3	14	2

* Average of five analyses by Marshall (1927, 1930).

coast, there are numerous sea stacks. From the cliff tops the land rises steeply by interlocking convex spurs to the central plateau above 400 ft. and then abruptly again by sharp ridges to over 1,000 ft. in Mt. Pitt and Mt. Bates in the north-west (see Plate I (*b*)).

A small area at Kingston and all of the 105-ft. high Nepean Island directly opposite, half a mile offshore, are composed of calcarenite, a limestone formed of consolidated current bedded calcareous sand, the remnants of a former much more extensive coral formation.

Carne (1885) has reported on the basalt, tuff, and limestone, the latter containing in the specimen analysed over 95 per cent. of the carbonates of calcium and magnesium. The sub-surface material of the Emily Bay calcareous sand has only 3 per cent. of material insoluble in acid and is very low in acid-soluble phosphorus (0·05 per cent.). An examination of the calcarenite revealed worn fragments of calcareous algae (Corallineae and a few *Halimeda*) bryozoa, foraminifera (*Marginopora*, *Cibicides*, *Eponides*, *Amphistegina*, *Sigmoidella*, *Triloculina*, &c.), and molluscan shell fragments. It is a shallow-water deposit in which terriginous material is represented by well-rounded grains of weathered vesicular basaltic rock and boulders of the same at the base of the formation (see Plate II (*a*)).

Behind the calcarenite formation at Kingston, where it rises to a maximum height of 50 ft., there is preserved a short length of an earlier coastline composed of faceted spurs falling steeply to the lower level of the calcarenite (see Plate II (*b*)). It is also partially preserved for a short distance above the cliffs between Kingston and Collins Head to the east.

With only one exception the streams of the island reach the sea either by falling precipitously over the low points in the undulating edge of the cliffs or by a series of cascades. The exception, Watermill Creek, entering the sea at Kingston is, in its lower course, a mature gently graded stream for about 1 mile. It is characterized by a significant accumulation of alluvial soils and swamps and traverses the limestone area for the lower third of that distance. Three other streams discharging on the south and west coasts contain short mature swampy reaches above where they discharge over the cliffs (see Fig. 1). These formations may represent a former base level of erosion between 100 and 200 ft. above present-day sea-level, and are, perhaps, to be correlated with the cliff benches and sea stacks on the north coast.

The Soils and their Relationships

Table 2 shows the soils mapped on the island, their classification into krasnozems and other soils, and their relation to topography, drainage, and parent materials.

A full description of these soils and analytical data are given in Soils and Land Use Publication No. 12 and the following, including Table 3, is a summary of the important features of the soils.

Palm Glen clay

This soil is located on the upper and middle slopes of Mt. Pitt and Mt. Bates and along Stockyard Road to the northwest of Ball Bay. It lies on

TABLE 2

Soils Mapped on Norfolk Island

Great soil group	*Soil series and type*	*Topography and drainage*	*Parent material*
Krasnozems .	Palm Glen clay	Steep to moderate slopes Unrestricted drainage	Basalt
	Mt. Pitt clay	Moderate slopes Unrestricted drainage	Basalt
	Rooty Hill clay	Steep to moderate convex slopes and ridge tops Unrestricted drainage	Basalt
	Steel's Point clay	Gently undulating to flat Unrestricted drainage	Probably tuff
	Middlegate gravelly clay	Gently undulating drainage divide Unrestricted drainage	Basalt
	Selwyn clay	Gently undulating areas on cliff tops Unrestricted drainage	Basalt
Skeletal soils .	Emily Bay calcareous sand	Undulating Unrestricted drainage	Calcarenite
	Unnamed shallow stony soils	Steep slopes Unrestricted drainage	Basalt
	Cliff formation	Very steep slopes Excessive drainage	Basalt and tuff
Alluvial soils .	Unnamed alluvial soils	Gently sloping to flat Unrestricted drainage	Basaltic alluvium
Acid swamp soils	Unnamed swamp soils	Valley floors with restricted drainage	Basaltic alluvium

moderate to steep slopes and for the most part is still under forest, being generally regarded as an inferior soil.

The surface soil consists of a dark red (2·5 YR 4/4), friable clay with organic matter and a pronounced granular to crumb structure. At less than 12 in. depth this is underlain by a deep subsoil of red (10 R 4/5–4/6), somewhat compact but friable, granular clay in which decomposing basalt appears at a depth of about 60 in. and increases in quantity with depth.

Mt. Pitt clay

This chocolate-coloured soil is located on the middle and lower gentle to moderate slopes of Mt. Pitt and Mt. Bates and north of Ball Bay. Generally it has been cleared for pasture and is also used for horticultural purposes. It is regarded as a moderately good soil.

The surface soil consists of about 12 in. of dark red-brown (2·5 YR 3/3), friable clay containing organic matter and with a nutty structure. This passes into a deep, friable clay, red-brown (2·5 YR 4/4) in colour and with a granular structure.

Rooty Hill clay

This soil occurs most intensively on the dissected slopes and spurs of the eastern and central part of the island. It is also found wherever the streams cut deeply into the land in the vicinity of the cliffs.

The surface soil is a dark brown (7·5 YR–10 YR 3/2), friable, nutty to granular clay generally less than 12 in. deep. It rests on a subsoil of red-brown (5 YR 4/5), friable, granular to crumb-structured clay generally with concretionary material in the lower portion. At depths ranging up to 4 ft. weathered basalt appears and rapidly increases with depth.

Steel's Point clay

This soil, regarded as the most fertile arable soil on Norfolk Island, occurs most extensively near Steel's Point, not so extensively near Duncombe Bay, and in a broken area near Rocky Point. It occupies nearly flat to gently undulating sites and is favoured for all horticultural crops, especially bean seed production.

The surface soil is a dark brown (10 YR 3/2), friable, crumb- to granular-structured clay with organic matter; it gradually changes to a dark yellow-brown colour (10 YR–7·5 YR 4/3) with depth. At about 30 in. there is a gradual change to a reddish- to yellowish-brown (5 YR 4/5–7·5 YR 5/5), friable, indefinite crumb- to granular-structured clay.

Middlegate clay

This soil occupies the least dissected central portion of the island in the Middlegate and Burnt Pine areas. It occurs on gently sloping to flat sites on what appear to be remnants of an elevated tableland. This topographic position and the occurrence of fine pisolitic ironstone gravel in the surface horizons of the soil indicate a greater age and degree of maturity for this soil than for other soils of the island.

The surface soil is a nearly black (2·5 Y–10 YR 3/1), friable, nutty clay containing slight to moderate amounts of a fine, rounded, ironstone gravel which increases with depth to about 10 in. Below is a red-brown (5 YR 4/4), friable, crumb-structured clay to a depth of about 24 in., below which a darker red-brown (5 YR 3/2–3/4), friable, crumb-structured clay occurs with some concretionary material in the lower portion. This persists to depths of about 50 in., below which weathered basalt increasingly occurs.

Selwyn clay

This soil is found on gently undulating areas on the top of the cliffs on the west coast of the island. It is not extensive and persists for only a few chains inland. There is an association of sooty petrel burrows with this soil and the birds' habits in burrows may be responsible for the remarkably uniform and dark colour of the whole profile of this soil. It is regarded as a very fertile soil but occurs in rather badly exposed situations.

The whole profile to the C horizon is a dark brown (7·5 YR 3/2), friable clay, nutty to granular in structure for a depth of about 20 in., then

becoming indefinite crumb-structured. At about 60 in. slight decomposing basalt occurs and increases with depth.

Emily Bay calcareous sand is a shallow skeletal soil, the parent material of which was most recently exposed and which is being continually and rapidly leached away quite apart from its rapid dispersal by marine erosion. The residue after leaching is partly derived from the less soluble material of the calcarenite proper and also partly, and probably much more greatly, from the included terrigenous material, especially as solution and weathering reach down to the base of the formation. The accumulated residue forms a shallow soil of limited use.

TABLE 3

Descriptive Analytical Data for Soils

Soil type	*Sample no.*	*Depth (in.)*	pH	*Organic carbon* (%)	*Total nitrogen* (%)	*Total phos.* (%)	*Clay* (%)	*Exchangeable cations* (*m.e./100g.*)		
								Ca	Mg	K
Palm Glen clay	18883	0–7	6·0	5·1	0·49	0·20	69	6·1	4·4	1·0
	18885	12–30	4·9	1·7	0·12	..	77	2·0	0·2	0·2
	18887	56–66	4·7	0·7	0·04	0·09	55	..	..	..
Mt. Pitt clay	18878	0–7	6·7	5·1	0·51	0·09	62	13·3	4·3	1·1
	18880	14–27	6·4	1·8	0·08	..	82	4·0	3·4	1·4
	18882	50–72	6·0	1·1	0·05	0·06	64	..	..	..
Rooty Hill clay	18860	0–5	6·0	6·6	0·58	0·15	64	9·4	4·4	0·6
	18862	10–17	6·2	2·8	0·24	..	71	..	..	..
	18863	17–27	6·1	2·3	0·12	0·12	63	2·9	1·4	0·3
	18900	0–10	6·9	5·3	0·47	0·15	58	10·0	4·8	0·4
	18902	19–30	5·6	2·3	0·14	0·12	80	2·4	0·7	0·2
Steel's Point clay	18872	0–7	7·1	3·7	0·37	0·30	70	15·4	5·2	0·5
	18874	18–31	7·5	1·6	0·15	..	79	7·5	4·2	0·1
	18876	44–58	5·9	1·7	0·09	0·12	86	2·1	2·7	0·1
	18889	0–6	7·4	4·4	0·48	0·32	68	21·6	7·1	1·5
	18891	12–29	7·9	1·4	0·15	0·20	74	7·4	4·0	0·5
Middlegate clay	18865	0–4	5·9	4·9	0·41	0·08	39	6·2	1·8	0·5
	18867	10–23	5·8	3·6	0·15	..	85	4·6	1·3	0·1
	18869	32–38	5·1	2·5	0·08	0·07	86	..	..	..
Selwyn clay	18894	0–7	7·0	5·5	0·47	0·43	56	12·8	12·8	1·0
	18896	22–36	7·5	2·1	0·17	..	71	7·1	5·6	0·3
	18898	50–64	7·5	1·5	0·09	0·13	80	4·0	4·0	0·1

The age relationship of three of the more extensive soil types, namely Rooty Hill clay, Steel's Point clay, and Middlegate gravelly clay, has been investigated by comparing the results of chemical analysis of samples of

TABLE 4

Elemental Composition of Soils expressed as Ratio of Elements in Basalt

Soil type	*Middlegate clay*		*Rooty Hill clay*		*Steel's Point clay*	
Depth in.	0–4	32–38	0–10	19–30	0–6	12–29
Ca and Mg	0·05	0·01	0·05	0·01	0·07	0·03
Si	0·19	0·31	0·29	0·33	0·39	0·41
Al	0·72	1·3	1·7	1·7	1·2	1·1
Fe	3·4	3·2	2·7	2·8	3·0	3·1
Ti	13	2·5	3·0	2·5	3·5	3·0

these soils with the parent material, basalt. Table 4 shows the amounts of Ca and Mg, Si, Al, Fe, and Ti in the surface and subsurface of these soils expressed as a ratio of the amounts of these elements in the basalt (Table 1).

By expressing the results in this manner, the chemical changes that have occurred during the formation of the soils become readily apparent. Calcium and magnesium are representative of the elements rapidly lost in weathering and the amounts retained are very low, being essentially all associated with the exchange complex. Silicon is also lost, particularly when there is excess leaching, and it can be seen that all soils are low in silicon, with the Middlegate clay being noticeably lower than either the Rooty Hill clay or the Steel's Point clay. Iron and titanium, on the other hand, are retained in the profile and the figures for the Middlegate clay again reflect the greater maturity of this soil. Although it is not safe to place much reliance on individual figures in comparisons based on elemental composition of soils, consideration of all the figures in Table 4 indicate that the Middlegate clay might be at least twice as old as the Rooty Hill clay.

Compared with krasnozems from other localities, one of the outstanding features of the soils of the island, particularly the Steel's Point clay and the Selwyn clay, is their neutral or slightly alkaline reaction and the high exchangeable calcium (see Table 3). It has been shown (Stephens and Hutton (1954)) that for the greater part of the year there is an excess of rainfall over evapotranspiration and hence considerable leaching of the soils must occur. This should lead to acid soils low in exchangeable metal ions unless some other source has supplied calcium and magnesium. Air- or rain-borne oceanic salts would tend to add magnesium in excess of calcium, but as calcium is the dominant exchangeable cation oceanic salts do not appear to be the source. In their study of the soils of the Lower Cook Group, Grange and Fox (1953) have drawn attention to the fact that certain soils of this group of islands have received accessions of lime from coral sand used by the natives on the floors of their dwellings. Norfolk Island, however, was uninhabited when discovered by Captain Cook and there is no evidence of any former habitation.

The soils which contain the highest amounts of exchangeable calcium and magnesium are situated on the periphery of the island and it is possible that the cations may be from a former coral reef that once surrounded the island and could possibly have enveloped the present sites of the Selwyn and Steel's Point clays. The peripheral distribution and elevation of the soils suggest this.

Further evidence on the interrelationship of some of the soil types is given by the mineralogy of the clay fraction, and Table 5 gives the data for Middlegate clay, Rooty Hill clay, Steel's Point clay, and Palm Glen clay.

The presence of rutile and hematite in the surface of the Middlegate clay is in keeping with the morphological and chemical evidence that this is a very mature soil. Likewise the essential absence of free oxides from the Palm Glen clay indicates that this is one of the more juvenile soils of the island.

Although the minerals found in the clay fractions of these soils represent about 80 per cent. of the sample, they do not fully represent the mineral assembly of the soil as a whole. Some idea of the minerals of the

TABLE 5

Clay Mineralogy of Some Norfolk Island Soils

Soil type	*Middlegate clay*		*Rooty Hill clay*		*Steel's Point clay*		*Palm Glen clay*	
Depth, in.	0–4	32–38	0–10	19–30	0–6	12–29	0–7	12–30
Kaolin	mod.	much	much	much	much	much	v. much	v. much
Goethite	mod.	much	mod.	mod.	much	much	v. little	v. little
Hematite	mod.	little	..	..	..	..	..	..
Quartz	v. little	..	..	..	..	..	..	..
Gibbsite	v. little	..	little	little	..	..	..	..
Rutile	v. little	..	..	..	..	..	..	..

larger-sized fractions can be obtained from the chemical analysis of the whole soil and it would appear that in many of the samples, particularly those of Rooty Hill clay, gibbsite is the principal mineral in the coarser fractions. Gibbsite is also the dominant mineral identified in the concretionary material found in many of the soil types, and hence it would appear that in these soils aluminium oxide, set free during weathering, aggregates into particles greater than 2 μ.

The Geomorphic and Pedologic Succession

From a consideration of the preceding geological and pedological data a correlated sequence of events which governed the development of the soils of the island can be inferred. This sequence of events has exercised a considerable degree of control on the fertility of the soils as they are expressed today.

A comparison of the topography and soils of Norfolk Island with those of the Cook Islands makes it difficult to attribute the irregular topographic and soil features of Norfolk and its associated islands entirely to the activity of marine and atmospheric erosion on oceanic volcanic cones. If such was the case Norfolk Island might have been expected to resemble more closely the symmetrical islands described by Marshall (1927, 1930) and the subsequent soil maps thereof by Grange and Fox (1953). Although similar processes to those described by Marshall were unquestionably involved, if at different intensities, there is evident need to invoke additional geomorphic processes, namely, one or more of coastline faulting, volcanic explosion, makatea destruction and subsequent marine coastal erosion, and cessation of coral growth. The latter three are self-evident; volcanic explosion could account in part at least for the very lopsided and disorientated remnants of the cones on both Norfolk and Phillip Islands; and there is factual evidence of severe earthquakes and simultaneous coastal alteration in the early records of the islands, Maconochie (1844) stating that in 1793 two severe earthquakes altered the shape of Nepean Island and considerably widened the channel between it and Norfolk Island.

The sequence of geomorphic events that has led to the present-day soils of Norfolk Island is detailed below and illustrated as simply as possible in the cross-sectional diagrams of Fig. 2.

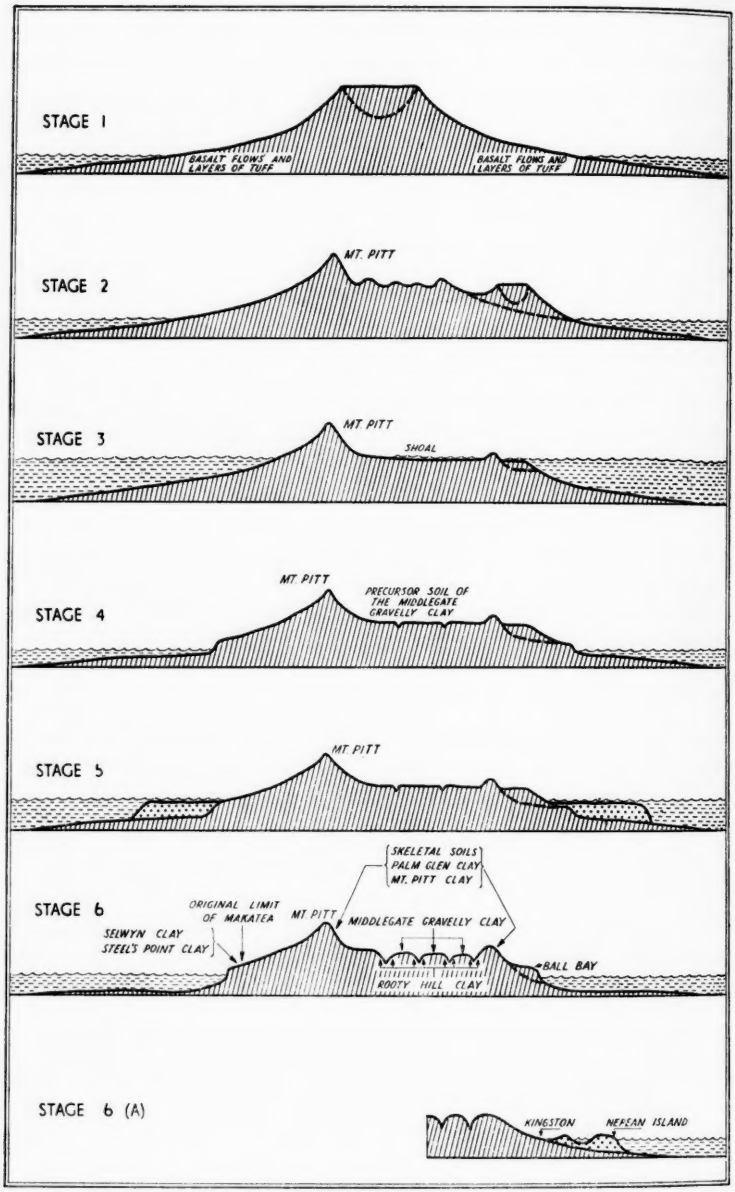

STAGE 1
BASALT FLOWS AND LAYERS OF TUFF
BASALT FLOWS AND LAYERS OF TUFF
STAGE 2
MT. PITT
STAGE 3
MT. PITT
SHOAL
STAGE 4
MT. PITT
PRECURSOR SOIL OF THE MIDDLEGATE GRAVELLY CLAY
STAGE 5
MT. PITT
STAGE 6
SKELETAL SOILS
PALM GLEN CLAY
MT. PITT CLAY
ORIGINAL LIMIT OF MAKATEA
MT. PITT
MIDDLEGATE GRAVELLY CLAY
SELWYN CLAY
STEEL'S POINT CLAY
BALL BAY
ROOTY HILL CLAY
STAGE 6 (A)
KINGSTON
NEPEAN ISLAND

FIG. 2.

Geomorphic Succession

I. Original marine volcanic cone on the Norfolk Ridge, composed of basalt flows and layers of tuff. Initiation of radial stream pattern. Probably pre- or early Tertiary.

II. Reduction of the cone by atmospheric erosion, assisted probably by a volcanic explosion, but leaving an arc of the crater rim (now Mt. Pitt and Mt. Bates). Development of parasitic cone. Initiation of non-radial streams dissecting main crater site.

III. Relative rise in sea-level, causing:

(*a*) The breaching of the parasitic cone (now Ball Bay).

(*b*) The development of a shoal between two islands composed of fragments of the rims of the main and parasitic craters.

IV. Retreat of the sea to near present-day level, causing:

(*a*) The exposure of the shoal as a tableland on which the precursor soil of the present-day Middlegate gravelly clay developed.

(*b*) The initiation of dissection leading ultimately to the present-day stream pattern.

(*c*) Marine erosion of the coastline, a section of which is preserved today in the steep but smooth spurs behind Kingston and remnants of which are preserved on top of the cliffs between Kingston and Collins Head.

V. (*a*) A rise in sea-level of over 100 ft. and the accompanying growth of a fringing reef. Aggrading and swamping of lower courses of island streams, particularly on west and south coasts (probably Miocene).

FIG. 2. Diagrammatic series showing the various stages in the development of the topography and soils of Norfolk Island (NW.–SE. sections).

Stage 1. Original marine volcanic cone on Norfolk Ridge.

Stage 2. (*a*) Reduction of the cone by atmospheric erosion, assisted probably by a volcanic explosion.
(*b*) Building of a subsidiary cone.

Stage 3. Rise in sea-level, causing:
(*a*) breaching of subsidiary cone by the sea.
(*b*) Development of a shoal leaving remnants of crater rims as islands.

Stage 4. Retreat of the sea to near present-day level, causing:
(*a*) Exposure of the shoal as a tableland on which the precursor soil of the Middlegate gravelly clay developed.
(*b*) Initiation of dissection of the tableland.
(*c*) Marine erosion of the coastline.

Stage 5. (*a*) Rise in sea-level of about 100 ft. and the growth of a fringing reef.
(*b*) Retreat of the sea (not shown) leaving a makatea around the island.

Stage 6. (*a*) Entire destruction of the makatea except for Nepean Island and near Kingston (see Stage 6 (A) below).
(*b*) Renewed marine erosion of the coastline.
(*c*) Accelerated dissection of the tableland giving rise to present-day topography, drainage, and soils.

Stage 6 (A) Part section from tableland to Nepean Island, showing remnant of makatea and of old coastline without cliffs preserved at Kingston and Nepean Island.

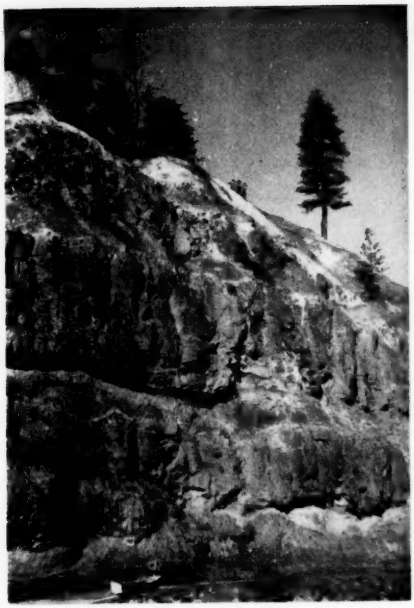
(*b*) Retreat of the sea leaving a makatea around the island, in places at least a mile wide and over 100 ft. high (Nepean Island, a remnant of the makatea off Kingston, is 105 ft. high).

VI. (*a*) Entire destruction of the makatea by atmospheric and marine erosion except for the small fragments remaining at Nepean Island and Kingston, the latter protecting an arc of former shoreline (see IV (*c*)) (Pleistocene and Recent).

TABLE 6

Paleopedology of Norfolk Island Soils

Palm Glen clay . .	Early or pre-Tertiary exposure: always unrestricted drainage: effects of prolonged leaching counteracted to a large extent by natural erosion of the steeply sloping situation.
Mount Pitt clay . .	Early or pre-Tertiary exposure: always unrestricted drainage: effects of prolonged leaching counteracted to a large extent by natural erosion of the moderately steeply sloping situation.
Middlegate gravelly clay .	Middle Tertiary exposure on elevated but rather flat surface with some restricted surface and temporarily restricted internal drainage: leaching continuous and intense with little or no rejuvenation due to erosion.
Steel's Point clay . .	Pleistocene exposure on gently sloping sites: always unrestricted drainage and leaching, the latter significantly counteracted by accession of materials from a former makatea and possibly by slight erosion.
Selwyn clay . . .	Pleistocene exposure on gently sloping sites: always unrestricted drainage and leaching; the latter strongly counteracted by the burrowing activities of petrels and significantly by accession of materials from a former makatea.
Rooty Hill clay . .	Late Tertiary to Pleistocene exposure on strongly sloping sites: always unrestricted drainage and leaching, the effects of the latter being significantly counteracted by erosion caused by headward erosion and down cutting of streams.
Unnamed shallow stony soils on basalt	As for associated nearby soils, but erosion predominant over soil formation leaving but shallow stony soils.
Cliff formations . .	Late Pleistocene to Recent exposure to marine erosion: always unrestricted surface drainage and erosion on very steep slopes precluding significant soil formation.
Emily Bay calcareous sand	Late Pleistocene exposure; always unrestricted drainage and leaching.
Unnamed alluvial clay soils	Soil formation continuous by additions of eroded material.
Unnamed peaty swamp soils	Restricted drainage initiated in Pleistocene times of higher sea-level: peat accumulation dependent on maintenance of restricted flow of associated streams.



a. The cliff face at Cascades on the north coast of Norfolk Island showing the alternate flows of basalt and layers of tuff

b. Characteristic topography of the greater portion of Norfolk Island. The gently sloping skyline 300–400 feet above sea-level indicates the general elevation of the island away from the crater remnant of Mt. Pitt and Mt. Bates which rises to just over 1,000 feet

J. T. HUTTON AND C. G. STEPHENS—PLATE I

a. Water-worn vesicular basalt boulders exposed on the coast in the base of the calcarenite formation

b. This view from an approaching aircraft shows the section of old coastline behind Kingston which itself is situated on the calcarenite. A section of the cliff structure of the present-day coastline is in the left foreground and the lagoon and reef to the right

J. T. HUTTON AND C. G. STEPHENS—PLATE II

(*b*) Renewed marine erosion of the coastline to form present-day cliffs and truncated streams, possibly assisted by faulting.

(*c*) Renewed dissection of the tableland, giving rise to present-day topography, drainage, and soils.

Pedological Succession

Table 6 presents a concise tabulated statement of the pedological factors which, in association with the geomorphic succession described above, have given rise to the present-day soils.

Acknowledgements

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A PETROGRAPHIC STUDY OF TWO SOILS IN RELATION TO THEIR ORIGIN AND CLASSIFICATION

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Introduction

THE use of thin-section and microscopic techniques in the study of Australian soils has developed in recent years as a potential aid in determining processes of soil formation and assessing the importance of them in soil classification. It is not to be expected that all of the micro-structures observed in thin-section can be interpreted accurately at the present time, but it is hoped that as the number of observations on soil profiles increases and with associated chemical, physical, and clay-mineral studies, the genetic processes involved in soil formation will eventually be understood. This paper records observations on two soils whose parent material is of wind-blown origin and presumed initially to be of similar composition.

The Soils

The soils examined occur in an area dominated by red-brown earths on the coarser-grained parent materials and in the better-drained positions, and grey and brown soils of heavy texture on the finer-grained parent materials and in the poorer-drained positions. The land form is a broad low dome with slight undulations similar to numerous such formations found on the almost flat Riverine plain (Butler, 1950). They have been classified as the Tenningerie and Wamoon soil series (Taylor and Hooper, 1938). In the particular occurrence examined they are associated with deeper sandy soils of aeolian origin and both the soil types concerned have an aeolian origin or have been so influenced. They occur on the gentle eastern slopes of a sand-hill with the Tenningerie on somewhat higher levels and the Wamoon on flatter sites very slightly raised above the main plain surface. The Tenningerie sand has unrestricted internal and external drainage, while the Wamoon has less free external and restricted internal drainage. The climate of the region is semi-arid with an average annual rainfall of 15 in. with a slight summer maximum. The location of the sample sites is in the Murrumbidgee Irrigation Areas about 10 miles south-east of Griffith, N.S.W. The two sites are about $\frac{1}{4}$ mile apart in contiguous areas of the respective types.

Sampling and Techniques

The profiles were studied in thin-section by means of a petrological microscope. Thin-sections of the undisturbed soil were made from oriented soil blocks which were taken from the soil horizons exposed in a sample pit. The blocks were carefully lifted from the pit face, marked for

Field Descriptions

Horizon	*Tenningerie sand*	*Wamoon sand*
A_1	19 in. of dull brown (5 YR 5/6) sand; structureless with soft, brittle, pulverent consistence. The colour becomes slightly paler with depth from 6 in. Very gradual transition from 12 to 19 in. to:	12 in. of brown (7·5 YR 5/4) loamy sand; structureless with soft, brittle, pulverent consistence. Gradual transition from 11 to 12 in. to:
A_2	14 in. of pale brown (5 YR 6/6) sand; structureless with brittle, pulverent consistence. The colour becomes slightly paler with depth from about 28 in. Sharp, uneven transition at 33 in. to:	3½ in. of paler brown (5 YR 5/4) sand; structureless with brittle, pulverent consistence. Sharp, even transition at 15 in. to:
A_3–B_1	Absent.	1 in. of grey-brown (7·5 YR 5/3) sandy clay loam; structureless and finely vesicular with brittle, pulverent consistence. Gradual transition from 16½ to 17 in. to:
B_{21}	10 in. of red-brown (2·5 YR 4/8) sandy clay with yellow-grey (7·5 YR 4/4) and dark grey (10 YR 6/6) mottles; shear colour is bright brown. The structure consists of broad domes 24 in. in diameter and 9 in. in amplitude; the material within the domes is massive with irregular vertical and horizontal cleavages with clay films and roots on the cleavage faces. The consistence is hard, brittle, pulverent. The material is moderately sub-plastic.* Gradual transition through:	9 in. of greyish-brown (5 YR 5/4) heavy clay with grey (10 YR 5/2), yellow (10 YR 6/5), and red (2·5 YR 5/6) mottles; the shear colour is yellow. The structure consists of irregular prisms 1½ by 4 in. with dark grey staining on the vertical faces; the prisms break down readily into 1½ in. blocks and more difficultly into ½ in. blocks. The consistence is hard, crumbly. Gradual transition at 26 in. to:
B_{22}	10 in. of similar material which changes gradually throughout its depth to 53 in. to:	10 in. of similar material with the amount of red mottle decreasing, the texture becoming slightly coarser and the structure better developed to strong grade, sub-angular blocky. The material is slightly sub-plastic. Gradual transition at 36 in. to:
BC(?)	Similar material of sandy clay loam texture. Continuing to 66 in.	6 in. of brown (7·5 YR 5/4) medium clay with grey (2·5 Y 6/2) and red (5 YR 5/6) mottles. The structure is medium grade subangular blocky (2 in. blocks) breaking down to ½ in. blocks; hard, crumbly consistence. The material is slightly sub-plastic. There are low amounts of soft carbonates on the structure faces. Gradual transition from 42 to 48 in. to:

* Sub-plastic soil materials show an apparent increase in clay content with continued manipulation during assessment of field texture.

Field Descriptions (contd.)

Horizon	*Tenningerie sand*	*Wamoon sand*
C(?) .	..	15 in. of brownish-grey (7·5 YR 6/5) medium clay with grey (2·5 Y 6/3) mottles. The structure and consistence are the same as for the BC horizon. There are slight amounts of soft carbonates on the structural faces.

their orientation in the field, and packed in brass tins. The surface horizons of both the profiles lacked sufficient coherence for blocks to be handled safely, so they were sampled by means of a 4-in. Coile sampler. In the laboratory, oriented chips of suitable size for thin-sectioning were made from the blocks by carefully picking and scraping with a sharp scalpel. Because of the strong-grade, rather fine, structure of some of the soil horizons, great care had to be exercised during this phase of the preparation to prevent disturbance of the soil aggregates in the chips. It was found that even the sandy A horizons could be treated in this way if handled with extreme caution. The chips were then oven-dried at 105° C. and immersed in a plastic, Plastrene 47, in tubes of 1 in. diameter, evacuated for 30 min., allowed to set (about 2 hours), and finally cured at 70° C. The excess plastic was then filed away and the thin-section cut in the normal way except that the grinding was done entirely with dry carborundum powder.

In addition to the thin-section studies X-ray analyses of the clay-size fractions, bulk-density measurements, and spot chemical tests for manganese were made on samples from several horizons of both profiles.

Petrographic Examination

The detailed description of the petrographic examinations follows:

Horizon	*Tenningerie sand*	*Wamoon sand*
A_1 .	Micrograph 1. The mineral material consists of 90 per cent. by volume of primary mineral grains and 10 per cent. secondary clay materials. Grain size is coarse and very uneven (1·0 mm. to less than 0·02 mm.). Quartz is the dominant primary mineral with associated weathered felspars (microcline, plagioclase, orthoclase), weathered biotite, hornblende, black iron oxide, and small quartzite grains. Specific-gravity separations (bromoform at S. G. 2·83) enabled identification of the accessories rutile, ilmenite, leucoxene, anatase, zircon, sillimanite, andalusite,	Similar in most respects to Tenningerie sand except that the coatings on the primary grains are thinner and less continuous.

Petrographic Examinations (contd.)

Horizon	*Tenningerie sand*	*Wamoon sand*
	sphene, zoisite, epidote, and tourmaline (blue, yellowish - green, brown). All the primary grains are somewhat rounded; the plagioclase has frayed edges due to weathering along twin planes. In thin-section the primary grains are discrete with little or no clay or other material filling the interstices; this indicates loose packing. Practically all of the primary grains have thin coatings or organic and sesquioxide - stained, optically oriented clay minerals. This is weakly developed chlamydomorphic fabric of Kubiena (1938). The clay minerals are oriented with the C-axes perpendicular to the coated surfaces. The pore space is about 50 per cent. of the total area of the thin-sections. There is no well-developed microstructure.	
A_2 .	The only difference from the A_1 horizon is that the secondary clay minerals are slightly paler because of less organic staining.	Similar in most respects to Tenningerie sand except that the coatings on the primary grains are thinner and less continuous.
A_3–B_1 .	Absent.	Variable. The primary minerals are similar to those of A_2 horizon in kind, grain-size distribution, degree of rounding, and weathering, Over much of the slide there is practically no coating of oriented clay layers on the primary grains: the interstices are largely filled with dark coloured, almost isotropic, finely divided clay material (micrograph 2). There are small aggregates of optically oriented clay minerals in this dark material. This approaches the porphyropectic fabric of Kubiena. The pore space is small in size and amount. This kind of fabric grades into smaller areas which are almost identical with the A_2 horizon and into other small areas where the interstices between the primary grains are filled with strongly oriented sesquioxide-stained clay.
B_{21} .	Micrograph 3. The primary mineral grains are as for the A_2 horizon; muscovite is an additional pri-	Micrograph 4. The primary mineral grains are as for the A_2 horizon. Primary minerals are about 35 per

Petrographic Examinations (contd.)

Horizon	*Tenningerie sand*	*Wamoon sand*
	mary mineral. Primary minerals are about twice the volume of secondary clay minerals. All the primary grains and soil pore space are coated with thick layers of optically oriented clays; the coatings commonly coalesce, thus filling voids. This is strongly developed chlamydomorphic fabric. Other areas of the slide have a clay groundmass of various sized aggregates of oriented clays and a small proportion of unoriented clays; the primary grains in these areas have only very thin clay coatings and the pore space consists of fine irregular cracks with a few larger channels. A stringer of A_2 horizon material runs through the section. There are small aggregations of dark brown to black isotropic material associated with the soil pore spaces; tentatively, these have been identified optically as sesquioxides.	cent. by volume and secondary clay minerals 65 per cent. Unlike Tenningerie sand the groundmass is mottled in shades of yellow and brown with areas of patchy segregation of red sesquioxides. Coatings of clay minerals on primary grains are very thin and not highly oriented. This approaches porphyropectic fabric. The groundmass of secondary clay minerals contains only very small aggregates of oriented clays except in the areas of red sesquioxide concentrations, where larger aggregates have been formed and coatings on primary grains are similar to those in Tenningerie sand. Pore space is much less than in Tenningerie sand; it consists of fine irregular cracks about 0·05 mm. wide with a few larger ones. The fine cracks are commonly filled or coated with black, opaque isotropic material as in Tenningerie sand and the larger channels sometimes have oriented clays associated with them.
B_{22} .	The primary mineral grains are as for the B_{21} horizon, but not quite so rounded or weathered. The primary grains are heavily coated with oriented clays so that they are commonly joined together, but the interstices are usually not filled as they commonly are in the B_{21} horizon; thus the pore space is greater and pore size larger. There is less groundmass of partially unoriented clay material than in the B_{21} horizon. The dark brown isotropic material noted in the B_{21} horizon again occurs associated with cracks.	Similar in all respects to the B_{21} horizon except that the thin films of oriented clays on the primary grains and channel walls are even further reduced in thickness and are less strongly oriented.
BC .	Similar in all respects to the B_{22} horizon except for a further small decrease in the amount of secondary clay minerals and in the thickness of the sesquioxide-stained oriented clay coatings on the primary grains and walls of soil channels. There also seems to be a significant increase in the percentage of muscovite.	Similar in all respects to the B_{21} horizon except that the primary mineral grains have increased to about 50 per cent. of the total mineral material. In addition the groundmass is fairly even in colour and consists of very small aggregates of sesquioxide-stained, oriented clays with a few larger aggregates up to about 0·5 mm. in

Petrographic Examinations (contd.)

Horizon	*Tenningerie sand*	*Wamoon sand*
		diameter. There is less of the dark coloured, opaque, isotropic material.
C .	Not sampled.	Micrograph 5. Similar to the BC horizon except for more positive orientation of the clays in the groundmass; there is a greater percentage of fairly large aggregates and more positive orientation of the fine aggregates in irregular bands running through the sections. Pore space consists of fine irregular cracks with the associated dark brown isotropic material. The percentage of primary minerals has fallen to less than 30 per cent. of the total mineral material.

Bulk-Density Measurements

Bulk-density measurements* have also been made on selected horizons of the two soil profiles and the results are set out in Table 1.

TABLE 1

Bulk-Density Measurements

Horizon	*Tenningerie sand*	*Wamoon sand*
A_2 . . .	1·54±0·08	1·66[a]
B_{21} . . .	1·79±0·08	1·74±0·05
B_{22} . . .	1·67±0·08	1·73±0·01
BC . . .	..	1·80±0·06
C (?) . .	..	1·65±0·02[b]

[a] Single determination.

[b] Thin-section evidence strongly suggests that this layer does not belong to the soil profile—it is really a D horizon.

If the particle density remains constant throughout a profile then the bulk-density measurements give an indication of the variation in total porosity down the profile. Thus, in Tenningerie sand, total porosity is lower in the B_{21} horizon than in the upper or lower horizons. In Wamoon sand, the total porosity is highest in the A horizons, but does not change significantly below the B_{21} horizon except for the deepest horizon. The thin-sections confirmed both of these propositions (see micrographs).

* Bulk-density measurements made by A. V. Blackmore, Division of Soils, C.S.I.R.O.

Chemical Analyses

The results of the chemical analyses* are set out in Table 2. The profiles differ markedly in particle-size distribution in the B and lower horizons, Wamoon sand having about twice the clay content of Tenningerie sand in the upper B horizon. The exchangeable cations show a gradual rise in the proportion of sodium and magnesium with increasing depth. This trend is more marked in Wamoon sand than Tenningerie sand.

TABLE 2

Analytical Data

Depth (in.)	*Horizon*	pH	*Particle-size analysis (mm.)* % 2–0·2 *mm.*	0·2–0·02 *mm.*	0·02–0·002 *mm.*	0·002 *mm.*	*Total soluble salts* (%)	*Chloride* (NaCl)	*Exchangeable cations (m.e. %[a])* Ca	Mg	K	Na	H
Tenningerie sand													
0–6	A_1	6·1	66	22	5	4	0·017	0·003	2·4	0·5	0·49	0·03	2·9
6–12	A_1	5·7	63	26	4	4	0·015	0·002	..	..	..	..	..
19–23	A_2	6·8	62	27	3	5	0·006	0·002	2·0	0·6	0·14	0·08	1·7
28–33	A_2	7·3	63	27	3	5	0·008	0·003	..	..	..	..	..
33–43	B_{21}	7·9	48	16	3	30	0·043	0·018	7·4	3·5	1·4	0·84	1·6
53–61	BC	7·7	46	25	6	21	0·064	0·023	5·7	3·3	1·1	0·57	1·5
Wamoon sand													
0–6	A_1	5·8	59	28	5	6	0·006	0·003	1·1	0·7	0·39	0·09	4·4
6–11	A_1	5·2	57	29	5	6	0·012	0·001	..	..	..	..	..
12–15½	A_2	6·7	60	30	4	3	0·005	0·002	1·1	0·9	0·05	0·17	1·8
15½–20	A_3–B_2[b]	6·5	39	16	3	38	0·048	0·024	5·8	6·0	0·58	1·9	5·2
20–24	B_{21}	6·7	24	10	3	60	0·103	0·051	..	..	..	..	..
27–33	B_{22}	7·8	23	11	2	59	0·155	0·082	9·9	12·2	1·8	3·2	2·6
36–42	BC	8·8	31	17	3	43	0·187	0·068	..	..	..	..	..
48–60	C(?)	8·7	4	17	9	62	0·301	0·089	..	..	..	..	..

[a] m.e.%: milli-equivalents per 100 g. air-dry soil.
[b] Thin A_3–B_1 (1 in.) mixed with B_{21} material.

In addition, the finely disseminated, dark brown, isotropic material associated with the soil cracks was shown chemically to contain quite large amounts of manganese.† The amount of manganese present increased from the surface to the deeper horizons, there being only a trace at the top of the B horizons but moderately large amounts in the B_{22} horizons.

X-Ray Analyses‡

X-ray analyses of the $< 2\mu$ fraction from selected horizons were made and showed little variation in the mineral species or proportions in either profile. Illite is the dominant mineral and is, in general, present in about twice the quantity of kaolinite; small amounts of quartz are present in all horizons.

Discussion

The primary mineral species identified in each of the horizons of both profiles indicate that the parent material in each case was fairly uniform except in the deepest horizon of Tenningerie sand, where the percentage

* Analyses by standard methods as described by Piper (1947).
† Chemical test made by A. D. Haldane, Division of Soils, C.S.I.R.O.
‡ Analyses by K. Norrish Division of Soils, C.S.I.R.O.

of muscovite has increased significantly, indicating a slight change in depositional facies, and in the deepest horizon of Wamoon sand, where there is a sudden decrease in percentage of coarse primary grains and a change in fabric; this layer does not seem to belong to the Wamoon profile. The parent material of the soils has been described as being deposited as a wind-blown sand (Taylor and Hooper, 1938) and the rounding of the primary grains and the heterogeneity of the mineral species are consistent with such an origin, although both could be due to an earlier cycle of water deposition.

The micromorphology of the two profiles as seen in thin-section differs in three most important related characteristics. The B_{21} and lower horizons of Wamoon sand contain a high percentage of weakly oriented clay and the number of large pores is small; total pore space is low. In the corresponding horizons of Tenningerie sand there is much less clay and it occurs as strongly optically oriented layers coating the primary grains and pore spaces; total pore space is large in both size and amount.

The optical orientation of clay layers coating grains and pore spaces has been accepted by most observers as indicative of clay migration and deposition either by clay synthesis from solution or from colloidal suspension. McCaleb (1954) has suggested that it is due to surface-tension effects during deposition from colloidal suspension because of the direction of orientation of the clay grains with the C-axis perpendicular to the surface of deposition. This is consistent with the evidence of the thin-sections of the horizons of Tenningerie sand.

It is well known that many clay types will orient optically when deposited in the laboratory from colloidal suspension. Similarly it has been found that in mud puddles formed during rain a sedimentation sequence is formed on drying and in thin-section this sequence shows that the finest clay is strongly optically oriented, the coarser clay is partially oriented, and the silt is unoriented. There is no doubt that the strongly oriented finest clay layer was deposited from colloidal suspension. Observations made on thin sections of other profiles from near Griffith and from elsewhere in New South Wales (Brewer, 1955) have shown that, wherever the B horizons consist of dense clays of low permeability and small-sized pore spaces, there is no strong orientation of clay minerals into large aggregates or coatings, even though sesquioxides may have moved down the fine cracks. On the other hand, dense clay B horizons in which there are relatively few, but large, channels quite commonly have a coating of strongly oriented clay on the walls of the large channels. These observations support the suggestion that the oriented clays have moved as colloidal suspensions because of whose nature relatively large channels are necessary for movement and concentration. Whether oriented clay layers can be formed in soil profiles by synthesis from solution cannot be determined as yet.

It is apparent from the X-ray analyses of the clay-size fractions that clay type is not a factor determining whether illuviation can take place in these two profiles. It is noteworthy too, that the proportion of sodium in the exchange complex is greater in Wamoon sand, which has a minimum of illuviation, than in Tenningerie sand. This is contrary to what

would be expected, but it is possible that the Tenningerie profile did originally contain a higher proportion of sodium which has now been leached because of the relatively unrestricted internal drainage of the profile.

If this correlation of optical orientation and migration of clay is accepted, it can be concluded that the dominant genetic process in the development of the texture profile of Tenningerie sand is clay migration from the now coarse-textured A horizons into the sharply differentiated B horizons. On the other hand, Wamoon sand has only small proportions of oriented clay coatings in the B_{21} and lower horizons and some other explanation must be sought as the dominant process in development of the texture differentiation in this profile. It is suggested that this process has been a deposition of material from the surface of the Tenningerie sand sand-hill on to the surface of an originally thinner Wamoon profile.

While the mineral constitution of both parent materials may have had similarities there is evidence that the Wamoon B horizons have a different origin to any part of the Tenningerie profile and the Wamoon profile therefore consists of a younger formation now represented by the A_1, A_2, and A_3–B_1 horizons superposed on an older one represented by the B_{21} and lower horizons; there was probably some mixing of the two materials at the surface of deposition of the younger deposit. The A_3–B_1 horizon is more akin to a normal B horizon of the upper younger profile.

There are several observations which support these theses of the formation of Tenningerie and Wamoon sand:

1. The pattern of clay distribution in Tenningerie sand is what would be expected if clay migration were the dominant process, i.e. the amount of oriented clay and the total percentage of clay both decrease with depth in the profile from the B_{21} horizon. This applies to a lesser extent in the Wamoon profile except that the proportion of oriented clay is always low.

2. In both profiles the grain-size distribution and packing of the primary mineral grains is such that they would have remained very permeable throughout their history if the interstices were not filled. In Tenningerie sand, even in its present condition with thick clay layers on the mineral grains and pore-space walls, the interstices are not completely filled; it is still a highly permeable soil, which would facilitate clay migration. In Wamoon sand the interstices in the B horizons are filled with unoriented clay-size material and pore space is low.

3. The bulk density is at a maximum in the B_{21} in Tenningerie sand and then decreases significantly with depth while the observed pore space increases with depth (Mick, 1949; Brewer, 1955). In Wamoon sand bulk density and pore space both remain relatively constant with depth in the B_{21} and deeper horizons except for the lowest horizon, which is really a D horizon.

4. The thin coatings of stained, optically oriented clay minerals observed on the primary grains in the A horizons of both profiles indicate some deposition following migration even in these horizons, but since the coatings are no thicker in the A_2 horizons than in the A_1 horizons most of the mobilized clay must have been carried below the A_2 horizon. In

Wamoon sand this clay has formed thick coatings in patches in the A_3–B_1 horizon with only insignificant amounts in the B horizons. It seems, then, that in Wamoon sand permeability was sufficiently high only in the A horizons to permit significant clay migration and that the B horizons have been impermeable throughout their history of development.

5. The coarse-textured A horizons of Tenningerie sand have a total depth of 33 in. with an average of about 4·5 per cent. clay-size material while the B horizons sampled have a total depth of 30 in. with an average of about 25 per cent. clay-size material. Thus, if the original parent material had uniform clay content it would require only 13 per cent. to account for the clay-size material in the B horizons; the A horizons, therefore, could have supplied the clay-size material necessary for this profile development. In Wamoon sand, by the same kind of calculation, if the parent material had uniform clay content it would need to have about 35 per cent. clay-size fraction to explain the texture differentiation in the present profile. Assuming that the clay in the original parent materials was not strongly aggregated, then pore space in the Tenningerie material would probably be quite high whereas in the Wamoon material it would be relatively low, so that clay migration could be expected in the former but is much less likely in the latter. Similar calculations for the A horizons only of Wamoon sand indicate that a layer of surface material containing less than 8 per cent. clay would account for the clay still in the A_1 and A_2 horizons and all the oriented clay in the A_3–B_1 horizons.

All five of these observations on the Tenningerie profile support the thesis of clay migration as the dominant process in the formation of the texture profile. Observations 2 to 5 support the thesis of a subsequent deposition of material on an originally thinner Wamoon profile with later clay migration in the upper, coarser-textured deposit. The fact that these upper horizons are mineralogically similar to the lower horizons and to the Tenningerie sand horizons indicates that they were derived from the adjoining Tenningerie sand sand-hill. This occurrence of Wamoon sand lies entirely to the east of the Tenningerie sand and prevailing westerly winds would deposit Tenningerie material on it if for any reason, such as a slight change in climate, the Tenningerie sand sand-hill became unstable.

It is evident, then, that these two profiles result from very different processes and that clay migration requires reasonably good permeability in the solum. Conditions during the formation of Wamoon sand, since it received the deposit of Tenningerie material on the surface, were apparently suitable for clay migration since it has occurred in the A_1, A_2, and A_3–B_1 horizons, but this process was stopped by the impermeability of the B_{21} horizon, which shows optically oriented clay layers only where the pore spaces are unusually large. However, in both profiles the sesquioxides have been mobilized and translocated and the secondary deposits are highly manganiferous. There is no evidence of significant organic-matter migration in Tenningerie sand, but the very dark groundmass of the A_3–B_1 horizon of Wamoon sand may be due to organic staining.

It is significant that the present average annual rainfall of the area in which these soils are found is 15 in., with a summer maximum when evaporation would be high and percolation low. The fact that clay movement is found in the Tenningerie sand profile at a depth of at least 5 ft. is anomalous in view of these climatic conditions. It indicates that the soil profile is an old one and that its profile characteristics were developed under a past climate considerably more humid than the present. In addition, the probability of a wetter past climate, since the recent arid period (Browne, 1945), has been pointed out recently in regard to the occurrence of diatom skeletons and sponge spicules in the A horizons of many of the soils of New South Wales and Victoria (Brewer, 1955).

The major differences noted above in the micro-morphology of the Tenningerie and Wamoon profiles and particularly the striking difference in the degree of optical orientation of the clay in the B horizons indicates a major difference in genesis. Therefore, whether a classification is based on morphology or genesis such evidence derived from thin-sections should be considered. It fits with other morphological details which caused the original separation of the soils at a series level, but it also shows that these differences are far greater than was suspected from field examination. This fact, together with the suggested explanation of polygenetic origin of the Wamoon soil, provides a sound basis for separation in classification at higher levels.

Summary and Conclusions

1. Two soil profiles from the Murrumbidgee Irrigation area have been studied by means of thin-sections with supplementary X-ray, physical and chemical analyses.

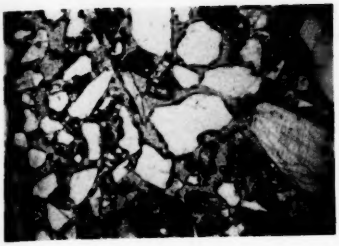
2. The parent materials of both soils are wind-blown sands and are fairly uniform in composition except for a slight change in depositional facies in the deepest horizon of the Tenningerie sand profile and a marked change in fabric and the proportion of primary minerals in the deepest horizon of Wamoon sand which indicate that this layer does not belong to the profile.

3. Thin-section characteristics, bulk density measurements, and other measurements show that the texture differentiation in the Tenningerie sand profile is due almost entirely to clay illuviation, whereas in the Wamoon sand profile, clay illuviation has been only a minor process. The thick A horizons of the Wamoon profile are probably due to surface accumulations from the Tenningerie sand profile.

4. Clay illuviation is probably due to movement in colloidal solution which took place under a more humid past climate.

5. Clay type is not a significant factor in the control of illuviation in these two profiles.

6. The sesquioxide concentrations in both soil profiles are quite highly manganiferous and have been translocated down the soil channels.



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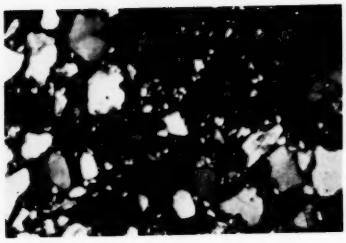

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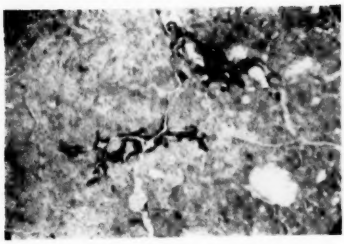

5

1. Ordinary Light. Magnification × 13. A_1 horizon of Tenningerie sand.

2. Crossed Nicols. Magnification × 13. A_3–B_1 horizon of Wamoon sand: dark, almost isotropic clay groundmass with small patches of strongly oriented clays.

3. Crossed Nicols. Magnification × 13. B_{21} of Tenningerie sand: strongly oriented clay layers enclosing sand grains.

4. Crossed Nicols. Magnification × 13. B_{21} of Wamoon sand: finely oriented clay groundmass with only very small areas of strongly oriented clay.

5. Ordinary light. Magnification × 13. Manganiferous sesquioxides deposited down fine cracks.

7. Thin-section studies are important as an aid in soil classification both from the morphological and genetic points of view.

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CHEMICAL CHARACTERISTICS OF TERRA ROSSAS AND RENDZINAS OF SOUTH AUSTRALIA

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Introduction

THROUGHOUT South Australia there occur areas of shallow, undifferentiated red and black soils overlying highly calcareous material. In many places they are found adjacent to one another over apparently similar calcareous material. Pedologists have classified these as terra rossas and rendzinas respectively.

Terra rossa is a term of Italian peasant origin, and considerable confusion surrounds its usage in soil science. It appears to have been used in the first instance by Zippe in 1853 (Kubiena, 1953) and since that time has been used to describe:

1. Red, shallow, undifferentiated soils 'developed on', 'developed from', 'overlying', and 'associated with' calcareous material.
2. The red material which remains after the weathering of limestone, and dolomite, and which is the parent material for new soils.
3. All the red soils of the Mediterranean region.

Following Stephens (1953) the term is used here with the meaning of (1).

Rendzina is a term of Polish peasant origin applied to black, sticky clay soils associated with calcareous material. It appears to have been used in the first instance by Sibirzev in 1895 (Kubiena, 1953); since then it has been used to describe black to brown, shallow, undifferentiated soils 'developed on', 'developed from', 'overlying', and 'associated with' calcareous material.

For both groups the phrase 'associated with', which does not imply any particular pedogenic process, is preferable when describing the relationship between the soil and the underlying calcareous material.

Although some Australian examples of these soils have been described (Stephens *et al.*, 1941) little is known of their chemical characteristics. In order to determine these, and to establish whether any characteristic has a unique value or range of values which may be used to distinguish between the groups, eleven profiles from the vicinity of Adelaide, and eight from the Lower South-east of the state were sampled and examined.

Field Characteristics

Morphology. The terra rossas range in colour from red to brown. They are shallow, varying from a few inches to 2 ft. in depth with no visible horizon development. In the areas examined they range in texture from

sands to clays and show little change with depth. They have a pronounced structure which varies from granular to nutty. Carbonates are not usually present, and the soils pass abruptly to the underlying calcareous material, which at the junction with the soil material consists of a very hard layer, sometimes laminated, and varying in thickness from $\frac{1}{8}$ in. to several inches.

The rendzinas, except for their colour, which varies from black to dark brown, differ very little in their morphological characteristics from those of the terra rossas. Light textured types have not been observed, and granules of carbonates appear more frequently. Occasionally the concentration of this material is such that the lower parts of the soil are grey.

Distribution. These soils occur in three principal localities in South Australia, viz.: in the vicinity of Adelaide, in the Lower South-east (Counties Robe and Grey), and on Eyre's Peninsula. Near Adelaide they occur on the lower slopes of the western scarp of the Mt. Lofty Ranges, intermixed with members of other great soil groups such as red-brown earths, brown solonized soils, and black earths. In the main, they overlie 2 or 3 ft. of highly calcareous material, which is underlain by, and in many instances penetrated by the pre-Cambrian rocks (slates, shales, and quartzites) and Tertiary deposits which comprise the rocks of the area (David, 1950; Glaessner, 1953; Sprigg, 1942). Some of the more calcareous slates and shales are directly overlain by these soils. In the Lower South-east the soils are associated with the consolidated stranded coastal dunes (terra rossa and rendzina), the interdune corridors (water-table rendzina), and the Miocene fossiliferous limestone (terra rossa and rendzina). The formation and interrelationships of these geologic and physiographic features have been considered by Sprigg (1952). Fig. 1 shows the sites of the profiles examined in the present study. No profiles were examined from Eyre's Peninsula.

Climate. The climate of the two areas in which the soils were studied is characterized by a cool, wet winter and a hot, dry summer. As such it may be classified as Mediterranean. Prescott (1949) has correlated the index $P/E^{0.7}$ with the boundaries of the major soil groups of Australia. For the Adelaide locality the mean value for this index is approximately 1·2; it is thus within the red-brown earth and black earth zone ($0{\cdot}92 < P/E^{0.7} < 1{\cdot}70$). In fact, soils of the red-brown earth group have been observed over similar material to that described for the soils under investigation. This is probably due to locally wetter conditions offsetting the stabilizing effect of the high calcium environment.

For the Lower South-east, the mean value for the index is 2·0; this area thus lies well within the podzolic zone ($P/E^{0.7} > 1{\cdot}70$). Again, soils with some horizon development have been observed, particularly in the eastern portion of the area, where the soils are considerably older than those of the more western parts.

Chemical Characteristics

The samples were collected from pits, suitable road-cuttings, and quarries, and prepared for laboratory analyses using procedures similar to those described by Piper (1942).

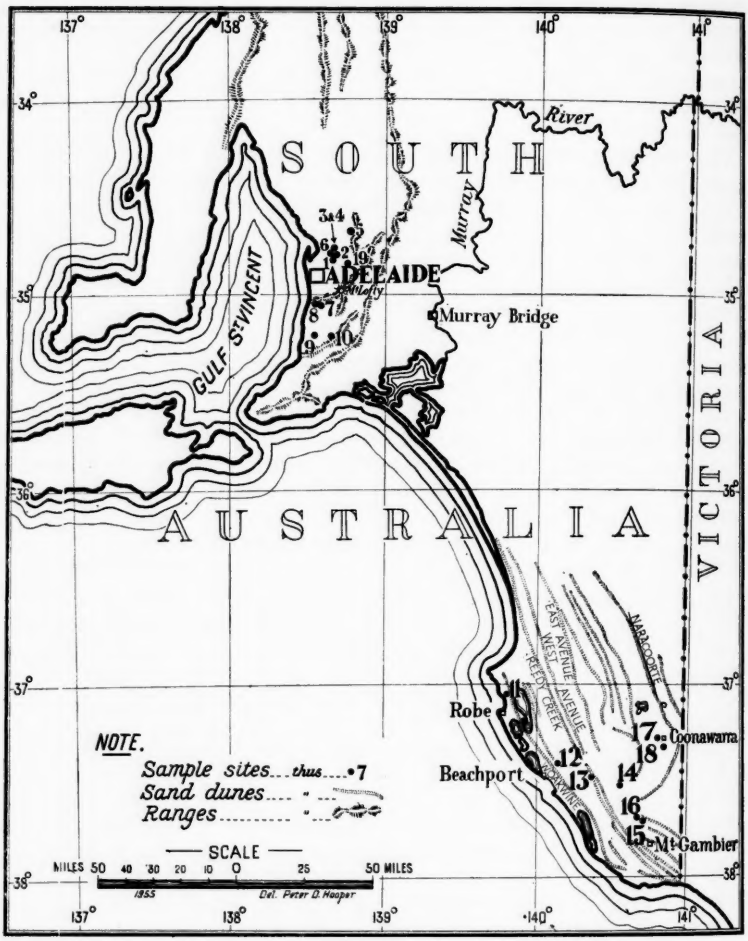

FIG. 1. Locality plan showing sample sites.

Methods

Reaction (pH) determinations were made on a 1 : 5 soil-water suspension, using the glass electrode and the technique of Raupach (1954).

Mechanical analyses were made by the international pipette method as given by Piper (1942) except that in order to bring about complete bleaching and removal of the organic matter, the treatment with hydrogen peroxide was carried out at pH 3 to 4, and repeated until two successive treatments produced no further change of colour in the residual material.

Phosphorus was that portion extracted by boiling the soil for 4 hours

with hydrochloric acid, and determined by a colorimetric method based on that of Berenblum and Chain (1938).

Free ferric oxide was determined using a modification of Jeffries's (1941, 1946) method developed by Haldane (priv. comm.); 2 g. of the soil ground to pass a 0·5-mm. screen or 0·5 g. of finely ground clay was treated with zinc dust and an ammonium oxalate-oxalic acid buffer (pH 3·8). The iron extracted was determined by reduction with stannous chloride, and titration with potassium dichromate.

Exchangeable cations were extracted by the method of Tucker (1954). Calcium and magnesium were determined by titration with the disodium salt of ethylene diamine tetra acetic acid, and sodium and potassium with a Beckman flame photometer.

For *ammonia adsorbed* the technique of Raupach (priv. comm.) was used; 1 g. of the soil, ground to pass a 0·5-mm. screen, was brought to equilibrium with ammonium acetate at pH 7·0 and centrifuged. The supernatant liquid was then decanted, the tube closed with a rubber stopper, and weighed. The contents of the tube were then transferred to a distillation flask, and after adding magnesium oxide the ammonia was distilled into boric acid, and titrated with standard hydrochloric acid. After applying a correction for the amount of ammonium acetate retained in the centrifuge tube, based on the difference in weights, the amount of ammonia adsorbed by the soil was calculated.

The remainder of the characteristics were determined by the methods of Piper (1942).

For the *statistical analyses* use was made of the tests described by Fisher (1950) for the comparison of two means. These tests were used to determine the level of probability (P) that the mean value of a given characteristic could be the same for the terra rossas and rendzinas.

*Results**

Reaction (pH). The distribution of the values for the surface and sub-surface samples is shown in Fig. 2. The diagram shows clearly that the range of values for the terra rossas overlaps, and may be considered

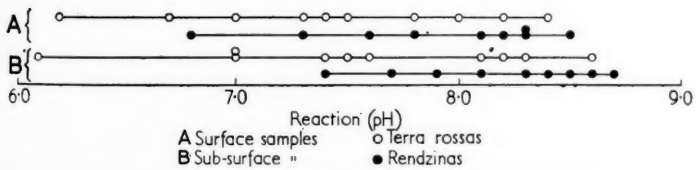

FIG. 2. Distribution of the values for the reaction (pH).

identical with that of the rendzinas. Of the twenty terra rossa samples shown only three have a reaction less than pH 7·0. Thus these soils, as they occur in South Australia, are not characterized by acid profiles.

* The morphological and chemical characteristics of each profile have been published in Division of Soils, Divisional Report 10/54, which is available on request.

Mechanical analysis. Fig. 3 shows the distribution of the values for the clay ($< 2\ \mu$) fraction, for the mineral portion of the surface and sub-surface samples. The figure shows the wide texture range—from sands to moderately heavy clays—over which the terra rossas are found, and also that the range of values for this group overlaps to a considerable extent the range for the rendzinas.

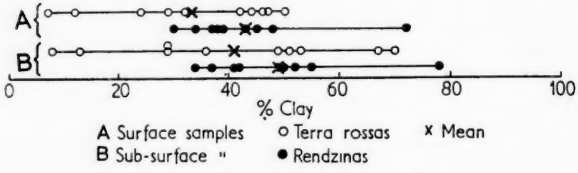

FIG. 3. Distribution of the values for clay.

Carbonate as $CaCO_3$. Of the ten terra rossa surface samples, nine have amounts less than the mean of 0·5 per cent. The remaining sample has 4·4 per cent. This profile (No. 11) is associated with calcareous dune sand, and is in an area of such dunes, many of which are bare of soil and vegetation; it is considered, therefore, that much of this material is accessory.

For the rendzinas, four have amounts varying from 2 to 11 per cent. The remaining five profiles have less than 0·5 per cent. Similar amounts are found in the sub-surface samples, so that it is apparent that calcium carbonate is not a necessary component of rendzinas.

Organic carbon and nitrogen

(*a*) *Organic carbon.* While there is no sharp separation, there is a tendency for the rendzinas to be higher in organic matter than the terra rossas. This is less marked in the surface than the sub-surface samples, as may be seen from Fig. 4, which shows the distribution of values for

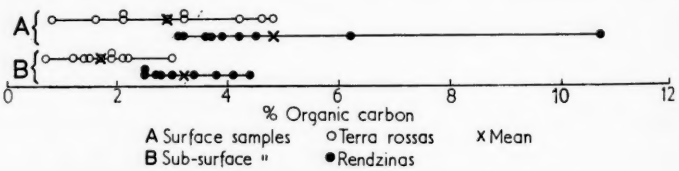

FIG. 4. Distribution of the values for organic carbon.

organic carbon for the surface and sub-surface samples. The mean value (4·8 per cent.) for the surface samples of the rendzinas has been influenced by the two samples with high contents of organic matter; the remainder of this group all fall within the upper part of the range (0·8 to 4·8 per cent.) of the terra rossas. The difference in organic carbon in the sub-surface samples of these two groups of soils has been brought out in the value for P, which has changed from 0·05 for the surface samples to 0·001 for the sub-surface samples. Nevertheless a small overlap is still observed.

(*b*) *Nitrogen.* The distribution of values for the surface and sub-surface samples is shown in Fig. 5. The patterns are very similar to those for organic carbon, and the difference in nitrogen content between the two sets of samples is reflected in the value of P, which has changed from 0·2 for the surface samples to 0·001 for the sub-surface samples.

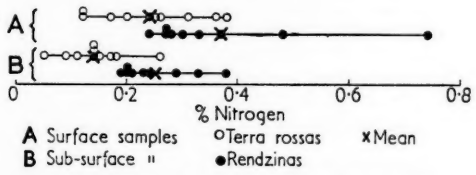

FIG. 5. Distribution of the values for nitrogen.

(*c*) *The interrelationship of carbon and nitrogen.* For the surface samples the values for the C:N ratio for the terra rossas vary from 6·8 to 14·0 with a mean of 11·9; for the rendzinas the range is 11·9 to 14·4 with a mean of 13·0. Corresponding figures for the sub-surface samples are 8·0 to 13·6 with a mean of 11·7, and 10·6 to 17·7 with a mean of 13·2. These values may be compared with the corresponding ratios found by Piper (1938) for the red-brown earths in South Australia. He noted a range of 6·2–13·9 (mean 10·1) for the surface samples and 4·8–13·3 (mean 8·5) for the sub-surface horizons.

Further information on the relationship of these characteristics may be obtained from the lines of regression of N on C, the equations for which are given in Table 1. The closeness of the linear relationship is clearly

TABLE 1

Equations for the Lines of Regression of N *on* C

	Terra rossa			*Rendzina*		
Samples	*Equation*	*Level of sig. 'b'*	*r*	*Equation*	*Level of sig. 'b'*	*r*
Surface .	N = 0·0694 C+0·037	P = 0·001	0·98	N = 0·0659 C+0·049	P = 0·001	0·99
Sub-surface	N = 0·0850 C−0·005	P = 0·001	0·98	N = 0·0896 C−0·039	P = 0·001	0·96

indicated by the values for the correlation coefficients (*r*). The regression coefficients (*b*) for the surface and sub-surface samples are different for the terra rossas at the level P = 0·1, and at P = 0·05 for the rendzinas. This indicates that there is probably a difference in the nature of the organic fraction between the surface and sub-surface for each group; while there is no difference between the groups for either the surface or sub-surface samples.

Phosphorus. Fig. 6 shows the distribution of the values for the surface and sub-surface samples. This diagram shows the almost identical range for each group in both sets of samples. The mean value for surface samples of the terra rossas is 0·031 per cent., and that for the rendzinas 0·032 per cent. These may be compared with the value of 0·024 per cent.

for the red-brown earths (Piper, 1938), and 0·009 per cent. for the brown solonized soils (Prescott and Piper, 1932) of South Australia. The former have been developed from the same slates and shales which

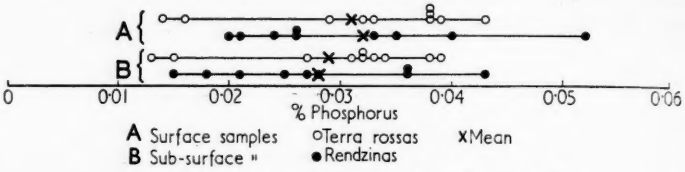

FIG. 6. Distribution of the values for phosphorus.

underlie the terra rossas and rendzinas of the Adelaide locality. However, the material underlying the brown solonized soils is of mixed origin, and has certainly passed through many complicated cycles of weathering and deposition (Crocker, 1946).

Free ferric oxide. Fig. 7 shows the distribution of values for the surface and sub-surface samples. Although the values for P (0·01 for the surface and 0·001 for the sub-surface) indicate that the means may be considered

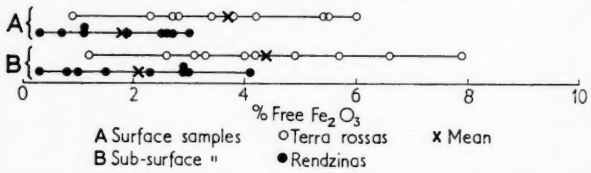

FIG. 7. Distribution of the values for free ferric oxide.

to be different, the above diagram shows clearly that the range of values for the terra rossas overlaps that for the rendzinas. Values for this characteristic cannot therefore be used as a criterion to distinguish between the groups.

Specific conductivity and chlorides. The mean values for the surface samples of the terra rossas are 0·8 mmhos. and 0·007 per cent. respectively, and for the rendzinas 0·13 mmhos. and 0·007 per cent. Similar values were found for the sub-surface samples. These indicate that soluble salts are not significant characteristics of these profiles.

Exchangeable cations. The mean proportions of the metal cations for each group are shown in Table 2. These figures show that the proportions of the cations adsorbed are very similar for both groups, with calcium the dominant cation amounting to approximately 80 per cent. The higher calcium environment of these soils may be contrasted with the red-brown earths of South Australia which show mean values of 61 per cent. for calcium and 24 per cent. for magnesium in the surface horizons (Piper, 1938).

Ammonia adsorbed. This characteristic may be considered a measure of the exchange capacity, and Fig. 8 shows the distribution of values for the surface and sub-surface samples. In general the rendzinas have a greater exchange capacity than the terra rossas. This is confirmed by the value

TABLE 2

Mean Proportions of Exchangeable Cations in Terra Rossas and Rendzinas

(Values expressed as % of Ca+Mg+K+Na)

Samples	*Surface*		*Sub-surface*		*Deeper*	
	Terra rossa	*Rendzina*	*Terra rossa*	*Rendzina*	*Terra rossa*	*Rendzina*
Calcium . .	79	81	79	82	78	76
Magnesium .	11	9	11	8	11	11
Potassium . .	8	9	8	8	8	10
Sodium . .	2	1	2	2	3	3

of P = 0·01 for both sets of samples. However, any such difference may not be considered a distinguishing feature, since the exchange capacity is dependent on such other characteristics as clay mineral assemblage and organic matter.

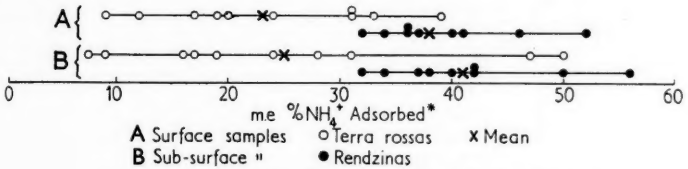

FIG. 8. Distribution of the values for NH_4 adsorbed.*

The colour in relation to free ferric oxide and nitrogen. Removal of the free iron oxides by the technique used here gave rise to grey or greyish-brown residues for the < 2-mm. samples and grey residues for the < 2-μ fraction. The 'redness' of the soil is thus related to these oxides, and in fact there is good agreement between the arrangement of the soil in order of 'redness' and the amount of free ferric oxide in the clay (< 2 μ) fraction. Oxidation of the organic matter by hydrogen peroxide left brown, red-brown, or red residues for all profiles except Nos. 13 and 17, for which the residues were greyish-cream. These two profiles also had low amounts (0·3 and 0·8 per cent. respectively) of free ferric oxide.

These observations point to the dependence of the colour of the soil on the free ferric oxide and organic matter present. Fig. 9 shows the relationship between nitrogen (used as a value for organic matter) and free ferric oxide associated with the clay (< 2 μ) fraction as percentages of the whole soil. This portion of the free ferric oxide, rather than the total, was used as it was considered that the iron oxide present in the finely divided form would have a greater colouring power than that found with the coarser fractions. For the majority of the samples 75 per cent. or more of the free ferric oxide is associated with the clay fraction. In Fig. 9 component samples of each profile are joined by lines, and the surface samples are suitably indicated. It is seen that, with few exceptions, the rendzinas lie above and the terra rossas lie below the line *OA*. The

* A measure of the total exchange capacity.

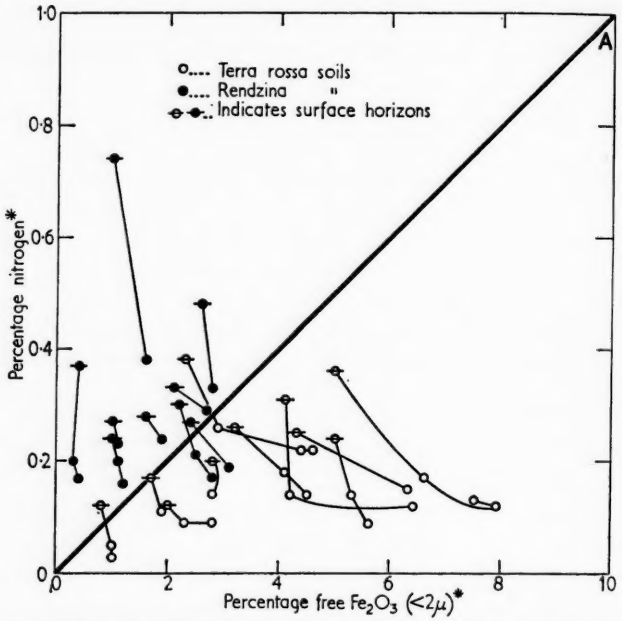

FIG. 9. Relationship between free ferric oxide (< 2μ)* and nitrogen.*

colour of these soils thus depends on the relative amounts of these two components rather than their absolute quantities. The line *OA* indicates a value of 10 for the ratio of free ferric oxide associated with the clay fraction to nitrogen. Thus, in general, the rendzinas have a value less than 10, and the terra rossas a value greater than 10. It is suggested that the value for this ratio, which may be called the 'colour index', offers a useful criterion to assist in the classification of the soils of these two groups.

If there is a close relationship between the colour of the soil and this index, then the arrangement of the samples in order of increasing redness should be matched by a steady increase in the value of the index. Such an arrangement is compared in Table 3 with the corresponding values for this index. A few surface and sub-surface samples have indices which are too high. The mineralogical examination (Norrish and Rogers, 1956) has shown that iron-bearing minerals other than the oxides of iron are present in the clay fractions of these samples. The principal such mineral is chlorite. While the method used for the determination of free ferric oxide is the best available, it is still not perfect in that some iron is extracted from these minerals. This causes the value for free ferric oxide, and the index derived from it, to be too high. Such samples are thus displaced in the direction of too high a colour index for their redness in the above sequence.

* As percentages of the whole soil.

TABLE 3

Terra Rossas and Rendzinas arranged in the Order of their Increasing Redness and compared with their Values for the 'Colour Index'

(% free Fe_2O_3 (< 2μ)*/% N*)

	Surface samples		*Sub-surface samples*	
	Sample no.	*Index*	*Sample no.*	*Index*
Increasing redness ↓	16470	1·3	16465	1·5
	16484	4·1	16485	5·5
	16464	1·1	16074	4·8
	16073	3·7	16471	4·3
	16479	5·4†	16480	8·5†
	16051	5·8	16052	8·0
	16122	6·4	16123	9·2
	16475	13†	16117	11
	16065	8·8†	16066	16†
	16060	12†	16127	12
	16116	6·1	16476	31†
	16126	7·5	16061	23†
	16452	6·0	16056	42†
	16055	17†	16070	20†
	16625	17†	16461	17
	16069	14†	16626	25†
	16460	10	16492	39
	16131	14†	16132	38†
	16491	21		

* Expressed as percentages of the whole soil.
† Sample contains chlorite.

Modification of Nomenclature

The few published analyses of extra-Australian examples of terra rossas and rendzinas are summarized in Table 4. For any one characteristic, this table shows that the range of values for either group overlaps that of the other. It is also seen that many of the values are similar to those reported here for South Australian examples.

The similarity of the chemical characteristics of these soils, and the steady progression in colour from black to red on the one hand, and black to grey on the other, suggests that there would be an advantage in considering each profile as a member of a sequence of soils. This sequence could be given individual status and subdivided into its red, brown, grey, or black members in a manner analogous to the subdivision of the podzolic soils into red, yellow, brown, and grey-brown. It is therefore suggested that all profiles having a shallow to moderately shallow solum with no marked textural differentiation throughout, and overlying calcareous material be designated *terracal* with a qualifying colour name to describe particular profiles, e.g. red terracal, brown terracal, black terracal. Such a grouping of the soils would be in conformity with the results presented here, and help to overcome the confusion surrounding the use of *terra rossa*.

TABLE 4

Chemical Characteristics of Extra-Australian Examples of Terra Rossas and Rendzinas

Characteristics	*Terra rossas*			*Rendzinas*		
	Min.	*Max.*	*No. of samples*	*Min.*	*Max.*	*No. of samples*
Reaction (pH) . .	7·2	8·4	11	5·4	8·5	20
	%	%		%	%	
CO_3 as $CaCO_3$ . .	0·6	37·0	7	1·5	93	31
Organic C . . .	0·5	2·6	3	0·7	15·3	10
Nitrogen . . .	..	..	..	0·08	0·5	14
Tot. sol. salts . .	..	..	..	0·03	0·19	20
	m.e. %	m.e. %		m.e. %	m.e. %	
Ex. cap. . . .	11·5	24·4	3	18	37	3

Summary

Ten profiles of terra rossas and nine of rendzinas from South Australia have been examined for their morphological and chemical characteristics. It has been shown that these characteristics are very similar for both groups, and that no one feature has a unique value or range of values which may be used to distinguish between the groups. The colour, the principal morphological difference, is largely dependent on the ratio of the free ferric oxide associated with the clay of the whole soil to the total organic matter. When per cent. nitrogen is used as a measure of the total organic matter, the value for this ratio, or 'colour index' as it may be termed, is, with few exceptions, less than ten for the rendzinas and greater than ten for the terra rossas. It is suggested that these soils are members of a continuous sequence, and that it would be more appropriate to group them under the one term *terracal* with a preceding colour qualification to describe particular members. Thus 'red terracal' would replace 'terra rossa'. The characteristics of two typical profiles are given.

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APPENDIX

A Typical Terra Rossa Profile

OF the terra rossa profiles examined it is considered that No. 18 (Coonawarra loam, Stephens *et al.*, 1941) represents an excellent expression of this group of soils. Located near Coonawarra in the Lower South-east of South Australia it appears to

overlie lake marls or similar calcareous deposits. This profile has also been illustrated by Stephens (1953, Fig. 19).

The morphological characteristics of the profile are given in Table 5 and the chemical characteristics of the solum are shown in Table 7. It is approximately neutral in reaction at all depths. Its mechanical analysis shows little evidence of profile development, and carbonate material is virtually absent. The data for the exchange complex show that this is highly saturated with metal cations, and dominated by calcium. The colour indices for the surface and sub-surface samples are 21, 38, and 60 respectively; they thus lie well to the red side of the figure of 10 proposed as the demarcation between rendzinas and terra rossas.

TABLE 5

Morphological Characteristics of a Typical Terra Rossa

(Profile No. 18)

Location . . .	Co. Robe, Hd. Comaum, Sect. 474. In an old quarry on western side of section.
Topography . .	Smooth gentle slopes at an elevation of 250 ft.
Description . .	16491: 0–4 in. red-brown (2·5 YR 3/6) soft loam with granular structure.
	16492: 4–11 in. red (2·5 YR 3/6) soft loam—sandy clay loam with nutty structure.
	16493: 11–18 in. red (2·5 YR 4/6) soft sandy clay loam—sandy clay with nutty structure. This is sharply separated from
	16494: hard calcareous material overlying
	16495: soft calcareous material.

A Typical Rendzina Profile

Of the rendzinas, No. 8 is considered to be a good representative profile. It is an example of these soils as they are expressed in the vicinity of Adelaide. The extent of this soil is not very great, and terra rossas overlying similar material occur within a short distance. This association of red and black soils in this locality is typical. The calcareous horizon, which is 2 to 3 ft. thick in this area, is underlain and interpenetrated by the banded slaty limestones of the Adelaide Series (Sprigg, 1942). Small pieces of these slates may be found throughout the profile; in the surface parts these are red and very hard, changing with increasing depth through brown to yellow-brown and becoming noticeably softer. These slates have thus contributed to the mineral fraction of the solum. The characteristics of this profile are given in Tables 6 and 7. The reaction is alkaline, and there is little evidence of horizon

TABLE 6

Morphological Characteristics of a Typical Rendzina

(Profile No. 8)

Location . . .	Co. Adelaide, Hd. Noarlunga, Sect. 472. South-west corner of section.
Topography . .	Moderate slopes at an elevation of 450 ft.
Description . .	16122: 0–4 in. near black (10 YR 3/2) friable clay with granular structure. Few carbonate granules.
	16123: 4–8 in. black (10 YR 3/2) friable clay with coarse granular structure. Few carbonate granules. This is sharply separated from
	16124: Irregular band, approximately 1½ in. thick, of greyish-white, hard, calcareous material. This passes to
	16125: Pinkish-yellow, soft calcareous material.

development. Carbonate material is present, but in small amount. The exchange complex is fully saturated, and is dominated by calcium. The colour indices for the two samples are 6 and 9 respectively, and they thus lie to the black side of the critical value of 10. This is in agreement with the visual estimation of their colours.

TABLE 7

Chemical Characteristics of a Terra Rossa and Rendzina Profile

	Terra rossa—Profile No. 18						*Rendzina—Profile No. 8*			
Sample no.	16491		16492		16493		16122		16123	
Gravel %	nil		nil		nil		2·8		2·9	
Reaction (pH)	7·4		7·5		6·9		8·5		8·7	
Mech. anal:	%	*	%	*	%	*	%	*	%	*
C. sand	8·3	9	8·6	9	7·3	7	1·6	2	0·9	1
F. sand	31·3	34	29·9	30	25·8	26	28·9	34	26·7	29
Silt	10·0	11	11·5	12	9·3	10	13·2	16	13·5	15
Clay	42·7	47	47·3	49	56·4	57	41·0	48	51·0	55
Loss on sol.	7·5	..	4·9	..	3·8	..	16·1	..	9·4	..
Total	99·8	100	102·2	100	102·6	100	100·8	100	101·5	100
	%		%		%		%		%	
Moisture	4·0		4·1		4·7		4·4		12·0	
CO_3 as $CaCO_3$	0·13		0·02		..		2·4		1·9	
Loss on igtn.	10·1		8·3		8·2		11·3		11·6	
Org. carbon	2·9		1·7		1·0		4·2		3·8	
Nitrogen	0·24		0·14		0·09		0·33		0·29	
Phosphorus	0·03		0·03		0·03		0·04		0·04	
Free Fe_2O_3	5·4		5·7		6·0		2·6		2·9	
Free Fe_2O_3 ($< 2\mu$)	11·7		11·3		10·0		5·1		5·3	
Acid sol. Fe	7·0		7·8		8·4		4·7		5·8	
Cl as NaCl	<0·01 mmhos.		<0·01 mmhos.		<0·01 mmhos.		0·01 mmhos.		0·01 mmhos.	
Sp. cond.	0·10		0·06		0·21		0·12		0·12	
Ex. cations:	m.e. %	*	m.e. %	*	m.e. %	*	m.e. %	*	m.e. %	*
Calcium	18·1	83	16·0	87	12·6	77	31·7	85	35·4	83
Magnesium	1·8	8	0·4	2	2·0	12	2·4	6	2·4	6
Potassium	1·8	8	1·6	9	1·4	9	2·5	7	2·8	7
Sodium	0·2	1	0·3	2	0·4	2	0·7	2	1·7	4
Total	21·9	100	18·3	100	16·4	100	37·3	100	42·3	100
NH_4^+ adsorbed	24·0		24·0		24·0		35·9		39·6	

* Percentage composition of the constituents.
m.e. % = milli-equivalents per 100 g. soil.

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THE MINERALOGY OF SOME TERRA ROSSAS AND RENDZINAS OF SOUTH AUSTRALIA

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Introduction

AN extensive study of the chemistry, mineralogy, and physical properties of a series of terra rossas and rendzinas occurring near Adelaide, South Australia, and in the south-east of the State has been carried out. Stephens *et al.* (1941) first described the South-east soils. Descriptions of and laboratory determination on the soils used in this investigation are given by Stace (1956) and Stace and Rogers (1954). McIntyre (1956) has investigated their physical properties and the relationship between these properties and iron and organic content of the soils. The clay mineralogy and the genesis of the soils are discussed in this paper.

Description of the Soils and Underlying Materials

In the south-east of South Australia the soils examined occur over marls and limestones, sometimes highly siliceous and of considerable thickness. Terra rossas and rendzinas also occur over the Miocene fossiliferous limestone in this area (Stephens *et al.*, 1941) but none of these were sampled. In the Adelaide area most of the soils examined overlie calcareous shales and slates of the Adelaide System (David, 1950; and Glaessner, 1953). The exceptions are profile 6 (rendzina) which overlies soft yellow calcareous clay which continues unchanged, at least, to the lowest depth of sampling (3 ft.), and profile 9 (rendzina) which overlies fine calcareous siliceous material containing bands of yellow and pink clay. In nearly all of the profiles there is an accumulation of secondary limestone at the base of the soil profile and this is capped by a thin band ($\frac{1}{2}$ to 2 in.) of hard consolidated limestone. A brief description of the geology of the underlying materials is given in Tables 1 and 2.

Experimental

X-ray diffraction powder and oriented flake techniques were used to determine the minerals of the clay fractions (less than 2 microns) of the soils and of the acid residues of the calcareous materials. The acid residues were prepared by removing carbonates with 0·1 N HCl. The flakes were examined air-dry and after treatment with glycerol (MacEwan, 1946). When chlorite or vermiculite was suspected, the clay suspensions were boiled with ammonium chloride and re-aggregated (Walker, 1951). In addition, the mineralogy of the underlying materials was determined by X-ray diffraction powder technique. Some of the clays were analysed by differential thermal method and the results were in accordance with those obtained by X-ray diffraction methods.

In Tables 1 and 2 the percentage total iron in the acid residues and underlying rocks was obtained with an X-ray fluorescent spectrograph.

The percentage of acid-soluble iron in the soils and of free iron in the clays was obtained by chemical methods and the figures quoted are taken from Stace and Rogers (1954). In some samples iron was estimated by both chemical and spectrographic methods and the agreement of the results indicated that the amount of acid-soluble iron was the same as the total iron.

Results

The results of the mineralogical examinations are given in Table 1 (south-east area) and Table 2 (Adelaide area).* The results obtained for the sub-surface soils only are given, typifying the profile, as their mineralogy was found to be essentially similar to the surface and deeper soils. The one difference that should be noted is that chlorite and montmorillonite occur only rarely and in small amounts in the surface soils although chlorite may be present in considerable amounts in the deeper horizons. The soils are listed in Tables 1 and 2 in order of increasing redness, as in the laboratory they were observed to grade from black through brown to red without a distinct division; some rendzinas are redder than some terra rossas! Despite this overlapping in colour, for the sake of convenience, the field classification has been retained. The percentage free Fe_2O_3 of the clay has been listed, as it is obvious from the tables that the colour (redness) of the soil depends largely on this. Because of this dependence and the relationship between colour and classification of the soils, attention has been focused, in this study, on the iron in the parent materials and in the soils.

(*a*) *Clay fraction of the soils*

Illite and kaolin are the dominant clay minerals of the clay fractions of the soils. Chlorite is generally found at lower depths in the redder soils from the Adelaide area. Some of the clay fractions (especially of the rendzinas) give intense central scattering in the diffraction photographs. This scattering was oriented in photographs of flakes and sharpened slightly on glycerol treatment. The exact nature of the clay giving this effect is not known but it is probably a randomly interstratified mica. Although the term is not strictly correct, it will be referred to as hydrated mica throughout this paper. In some photographs it is hard to distinguish between this mica and montmorillonite and they appear to grade into one another, pure montmorillonite being rarely found in the soils. In interpreting the photographs a sharp 10-Å line has been attributed to illite and a diffuse line at about 10 Å, coupled with central scattering, to hydrated mica.

The iron oxides identified were goethite and haematite. Radoslovich (1952), in a preliminary survey of these soils, identified magnetite in a magnetic separate from profile 2 (terra rossa, Adelaide area). It is possible that this mineral occurs in other profiles with high iron content.

* Detailed results of the materials examined are contained in a report (Stace and Rogers, 1954) copies of which may be obtained on request from C.S.I.R.O., Division of Soils, Waite Institute, Adelaide, South Australia.

TABLE 1

Mineralogy and Iron Content of Sub-surface Soils and Underlying Materials: South-east Soils

Profile no.	Mineralogy: Soil (< 2 μ fraction)		Mineralogy: Underlying limestone	Free Fe_2O_3 % of < 2 μ fraction*	Total Fe_2O_3 %: Soil*	Total Fe_2O_3 %: Acid residue limestone†	Underlying rocks
13 R	illite kaolin hydrated mica	m mo v.l	calcite illite kaolin montmorillonite	0·8	3·2	10·2	Lake marls of interdune corridors
17 R	illite kaolin hydrated mica	m mo mo	calcite	1·5	7·0	7·7	Lake marls of interdune corridors
14 R	illite kaolin hydrated mica	m v.l mo	calcite montmorillonite hydrated mica	3·5	5·4	6·8	Lake marls of interdune corridors
16 R	illite kaolin hydrated mica chlorite	m v.l v.l v.l	calcite montmorillonite illite kaolin	8·5	4·7	7·1	Consolidated stranded coastal dunes
15 TR	illite kaolin chlorite vermiculite goethite	l m v.l v.l	calcite kaolin chlorite illite	12·3	6·1	9·3	Consolidated stranded coastal dunes
11 TR	illite kaolin goethite	mo mo	calcite illite kaolin goethite or haematite	12·2	1·5	1·5	Calcareous shell sand
12 TR	illite kaolin chlorite goethite haematite	mo mo mo ? ?	calcite illite kaolin chlorite	15·2	3·6	2·5	Consolidated stranded coastal dunes; highly siliceous
18 TR	illite kaolin haematite	m l	calcite illite kaolin montmorillonite	11·3	7·8	7·5	Consolidated stranded coastal dunes

m = much; mo = moderate; l = little: v.l = very little; R = rendzina; TR = terra rossa

* Figures obtained by chemical analyses and taken from Stace and Rogers (1954). Analyst H. C. T. Stace.

† Figures obtained by X-ray fluorescent analyses.

Note. (1) Soils are listed in order of increasing redness, as estimated by eye, in the laboratory. (2) Quartz was found in all materials examined by X-ray diffraction methods. It has not been listed in the tables.

(*b*) *Underlying materials*

Where an appreciable amount of carbonate was present in the underlying rock, it was removed by treatment with 0·1 N HCl. In the Adelaide area the secondary calcareous horizon is distinct from the underlying rocks and results are given in Table 2 for each of these materials. In general, the minerals of the soils reflect those of the rocks underneath. The carbonate beneath the South-east soils and in the calcareous horizon of the Adelaide soils is calcite. The carbonate in the shales, &c., from the Adelaide area is mainly calcite but some dolomite has been found.

TABLE 2

Mineralogy and Iron Content of Sub-surface Soils and Underlying Materials: Adelaide Area Soils

Prof. no.	Mineralogy: Soil (< 2μ fraction)	Mineralogy: Secondary calcareous horizon	Mineralogy: Underlying rock	Free Fe_2O_3 % of < 2 μ fraction*	Total Fe_2O_3 %: Soil*	Total Fe_2O_3 %: Underlying rock†	Underlying rock
6 R	illite m kaolin mo hydrated mica mo	n.e.	calcite dolomite illite kaolin hydrated mica	2·8	4·2	6·2	Pliocene Marine Sands (?)—Soft yellow clay to depth of sampling = 3 ft.
1 R	illite m kaolin mo hydrated mica mo	calcite illite kaolin mont.	calcite illite kaolin goethite	6·2	4·5	8·8	Tertiary Lacustrine Series or Calcareous Shales of Adelaide System
8 R	illite m kaolin mo hydrated mica l	calcite kaolin illite mont. goethite	feldspar muscovite kaolin calcite v.l	5·3	5·8	5·9	Tapley Hill Slates of Adelaide System
4 R	illite m kaolin l hydrated mica l chlorite l	illite‡ chlorite	feldspar chlorite muscovite mont. kaolin	6·8	6·9	4·8	Tapley Hill Slates of Adelaide System
7 TR	illite m kaolin mo	n.e.	feldspar mica chlorite calcite l mont. illite kaolin	5·2	6·0	6·2	Tapley Hill Slates of Adelaide System
9 R	illite m kaolin mo	n.e.	jarosite calcite mont.	6·5	5·9	14·8	Tertiary deposits
3 TR	illite m kaolin l hydrated mica l chlorite l goethite	calcite feldspar? mont. illite kaolin	feldspar chlorite mica mont. illite l	6·4	8·1	5·8	Tapley Hill Slates of Adelaide System
5 TR	illite m kaolin ? chlorite mo haematite	calcite chlorite kaolin? mont.	feldspar calcite l chlorite muscovite illite	10·4	8·0	7·0	Tapley Hill Slates of Adelaide System
2 TR	illite mo kaolin mo hydrated mica l chlorite haematite magnetite	n.e.	feldspar dolomite chlorite muscovite illite	9·4	10·9	7·0	Tapley Hill Slates of Adelaide System
19 TR	illite m kaolin l chlorite v.l haematite	n.e.	n.e.	7·8	5·3	n.e.	Tapley Hill Slates of Adelaide System?
10 TR	illite m kaolin v.l chlorite mo haematite	n.e.	dolomite calcite chlorite mica mont. illite kaolin	13·1	10·2	4·2	Tapley Hill Slates of Adelaide System

m = much; mo = moderate; l = little; v.l = very little; R = rendzina; TR = terra rossa; mont. = montmorillonite; n.e. = not examined.

* Figures obtained by chemical analyses and taken from Stace and Rogers (1954). Analyst H. C. T. Stace. † Figures obtained by X-ray fluorescent analysis. ‡ Acid residue (< 2 μ) only examined.

Note. (1) Soils are listed in order of increasing redness, as estimated by eye, in the laboratory. (2) Quartz was found in all materials examined by X-ray diffraction methods. It has not been listed in the tables.

Discussion

(*a*) *Soils of the South-east*

The mineralogy of the clays of the soil and of the underlying calcareous material is consistent and suggests that the soils are residual. In addition, except for profile 13, there is a correspondence between total amount of iron in the acid residue of the calcareous material and that found in the soil. The low total iron values for profiles 11 and 12 reflect the siliceous character of these soils and their parent materials. Table 3 gives the mechanical analyses of some of the carbonate-free samples. There is good correspondence between the analysis of each soil and its parent material. Each soil shows some increase in clay with depth, the acid residue of the secondary calcareous horizon being markedly higher in clay.

All the results indicate that the soils are residual, their mineralogy, texture, iron content, and degree of redness being determined by the nature of the non-calcareous material in the limestone. It seems, therefore, that in the formation of the soils, apart from the loss of carbonate, mineralogical changes have been small. Where montmorillonite (or highly hydrated mica) is in the parent material it changes gradually to illite. This change, together with the weathering of chlorite where present, probably releases some iron to give free Fe_2O_3 in the soil.

There is a discrepancy between the iron values for the soil and the acid residue in profile 13 which has been classified as a ground-water rendzina. This soil may not be residual or, alternatively, iron may have been removed from it. Its location in an interdune corridor is such that surrounding sediments may have contributed to the soil; in addition its high water table could be effective in mobilizing iron.

TABLE 3

Mechanical Analysis of Soils and Underlying Rocks after Removal of Carbonate: South-east Profiles

Profile no.		*Surface soils*	*Sub-surface soils*	*Deeper horizon soils*	*Con-centrated calcareous horizon*	*Underlying rocks*
11 Terra rossa .	Coarse sand	53	60	57	28·6	60·9
	Fine sand	38	30	32	40·3	32·7
	Silt	2	2	2	5·2	0·9
	Clay	7	8	9	26·6	5·4
	Acid insol.	..	..	..	14·0	31·4
14 Rendzina .	Coarse sand	20	16	..	15·9	29·5
	Fine sand	29	26	..	21·2	18·1
	Silt	9	6	..	6·1	6·5
	Clay	43	52	..	60·3	48·3
	Acid insol.	..	..	..	5·9	15·3
16 Rendzina .	Coarse sand	22	21	..	1·5	not
	Fine sand	37	26	..	10·1	examined
	Silt	7	6	..	10·0	
	Clay	34	37	..	80·1	
	Acid Insol.	..	..	..	2·4	26·9

Analysed by H. C. T. Stace (Stace and Rogers, 1954).

From an examination of Table 1 it appears that rendzinas tend to form on the lake marls of the interdune corridors and terra rossas on the consolidated dunes. However, although terra rossas have not been found on the lake marls, soils of both groups occur on the consolidated dunes and the Miocene fossiliferous limestones in this area.

(*b*) *Soils of the Adelaide area*

Mineralogical data, Table 2, show that underlying rocks form the parent materials of the soils. With the exception of the two blackest soils (profiles 1 and 6) and profile 9, all the soils overlie Tapley Hill Slates of the Adelaide System. Chlorite is a dominant mineral of these slates and it appears to be the main iron-containing mineral. The surface soils contained little chlorite, suggesting that the free Fe_2O_3 content (and redness) of the soil is the result of the weathering of chlorite. In most cases the rocks contained only a little mica which, where it was appreciable, was identified as muscovite. Profile 9 has for its parent material a sediment containing much jarosite which, in weathering, would release iron. The total iron in the parent material is higher than would be expected on comparison with that in the soil. However, the weathering of jarosite would probably release soluble iron due to the presence of sulphate. The silicate minerals in the parent materials of the darker soils (profiles 1, 6, and 8) are illite, kaolin, and muscovite, which undergo relatively little change in forming the soils and therefore do not act as a source of free Fe_2O_3.

In most cases there is a limestone horizon beneath the soil which is considered secondary and has accumulated during the soil-forming process. It is not the parent material of the soil as has been suggested by Stephens (1953). The calcareous horizon is in most cases quite shallow and it is evident from its mineralogy (Table 2) that it is an intermediate between the soil and parent material and, therefore, is to be regarded as part of the soil profile. Mechanical analyses of the soils (Stace and Rogers, 1954) show a similar slight increase of clay with depth as do the South-east soils.

(*c*) *General*

There is very little difference in the clay mineralogy of the groups of soils from both areas. The rendzinas tend to contain more disorganized clay (hydrated mica) and the terra rossas more chlorite, the latter merely reflecting parent material. The redness of the soil is dependent on the amount of free iron oxide in the clay and this is governed by the amount of iron involved in the weathering of the parent rock. The larger amount of disorganized clay in the rendzinas, giving poorer drainage conditions, may be related to the small amount of free iron oxide in these soils (McIntyre, 1956).

Although the soils have been formed on very different parent materials —Tapley Hill Slates with little carbonate and limestones with more than 90 per cent. carbonate—the resultant soils are very similar. All the soils have a carbonate horizon which irrespective of parent material seems to perform the same role. It is the carbonate which gives all the soils

characteristics typical of terra rossas and rendzinas; that is shallow profiles with little differentiation. The presence of carbonate probably prevents clay movement and its chemical buffering action may slow down weathering of the parent material. In addition, the hard capping of the limestone layer will tend to keep the soil shallow by protecting underlying materials from weathering action.

Investigations of the clay mineralogy and the genesis of terra rossas and rendzinas from other countries have been carried out by various authors (Michaud *et al.*, 1946; Bramão *et al.*, 1950; Oakes and Thorp, 1950; Muir, 1951; Knox, quoted by Grim, 1953, &c.). Most of these workers show the influence of parent material as being of greater importance than climatic conditions while suggesting that there may be some loss from or enrichment of the soils during formation. The clays of these two groups of soils have been found to be variable; kaolin or illite are generally dominant, although occasionally large amounts of montmorillonite have been reported. Michaud *et al.* (1946) have identified palygorskite in terra rossas from the South of France, and Bramão *et al.* (1950) and other workers have found halloysite to be an important constituent in soils developed from limestone.

Summary

The mineralogy of a group of terra rossas and rendzinas occurring in the South-east and in the Adelaide area, South Australia, has been studied by X-ray diffraction methods. The clay mineralogy, the amount of iron, and the mechanical analyses of the soils and underlying materials show that the South-east group of soils is residual from the underlying calcareous rocks and that the Adelaide group is derived from the underlying materials which, in the main, consist of calcareous shales and slates of the Adelaide System. The amount of free iron found in the soils is related to the amount of iron present in the weatherable parent material. There is no sharp distinction between the mineralogy of the rendzinas and terra rossas. Illite and kaolin are the dominant clay minerals of the upper horizons of both groups. There is a tendency for the rendzinas to contain more hydrated mica than the terra rossas. Chlorite, as a residual mineral of the parent material, is generally found in the redder soils of the Adelaide area group.

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THE EFFECT OF FREE FERRIC OXIDE ON THE STRUCTURE OF SOME TERRA ROSSA AND RENDZINA SOILS

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Introduction

DURING chemical investigations of some terra rossa and rendzina soils from South Australia, it was found that if the soils of both groups were listed in order of increasing redness, there was a tendency for the free ferric oxide of the clay to increase and organic matter as indicated by total nitrogen to decrease (Stace, 1956; Norrish and Rogers, 1956). Since iron is considered to exert a strong aggregating influence under certain conditions, it seemed possible that in these soils iron could influence aeration in such a way as to affect the amount of organic matter; physical measurements were therefore carried out to test this theory. It had also been shown (Norrish and Rogers, 1956) that the mineralogy of these soils was similar, as was the exchangeable cation status (Stace, 1956), hence an ideal situation existed to investigate structure with respect to free ferric oxide and organic matter only. Only those soils were chosen where clay content was great enough to aggregate the soil strongly.

Methods

The profiles were sampled as near as possible to the position from which samples had previously been taken for chemical tests. The soil was air-dried in the laboratory where necessary, and macroporosity of aggregates (air space at 100 cm. water tension) was measured. To do this aggregates between 5 and 10 mm. in diameter were chosen, wetted for 3 days at a tension of 20 cm., and drained for a further 3 days at 100 cm. tension. The apparent density of each of ten aggregates was measured by the method of McIntyre and Stirk (1954), the mean particle density was found for each sample, and from these values total porosity calculated. From a second set of aggregates the water content at 100 cm. tension was measured. Subtracting this from the total porosity gave a value which is termed macroporosity.

Water-stability measurements were carried out on all soils. One set of soils was sampled at the end of a hot dry summer and another at the end of winter (the wet season in South Australia). The results obtained were therefore affected by the different moisture conditions at sampling as well as immediate past history and must be considered inconclusive. However, stability is high in all cases and in the latter group of soils there appears to be a possible relation between water stability and organic matter content (Clark and McIntyre, 1956). No relation with free ferric oxide was apparent in this case.

Results

Fig. 1 shows the plot of macroporosity against the percentage of free ferric oxide in the clay $< 2\,\mu$ (Stace and Rogers, 1954), this being considered more important than the free ferric oxide associated with total soil as far as structure is concerned. From the 20 samples on which measurements were made, 12 were from soils classified in the field as rendzinas and 8 from those classified as terra rossas. The complete plot of these soils shows an increase in macroporosity with the free ferric oxide content of the clay.

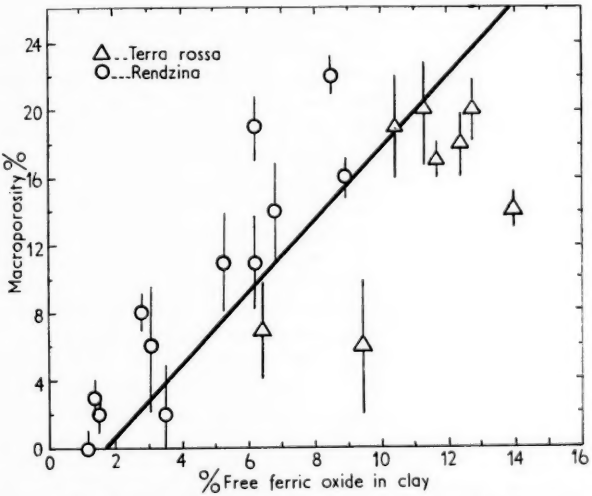

FIG. 1. Relation between macroporosity of the soil and free ferric oxide in the clay fraction.

A regression of macroporosity on free ferric oxide gives a regression coefficient which is highly significant ($P < 0{\cdot}001$). This significance is based on the assumption that the value of free ferric oxide obtained in chemical analysis is that of the sample taken for physical measurements. If this is so, replicates of free ferric oxide show that the error associated with its measurement is so much smaller than that associated with physical measurements that only the latter error need be used in significance tests. However, samples for physical measurement were sometimes taken from a nearby position rather than from the exact spot sampled for chemical tests, so that the free ferric oxide value for each soil is representative of a site rather than of a sample, and as such its associated error is unknown. Presumably, if it were known and used in significance tests, a lower level of significance would be obtained, but an extremely large error would be necessary to reduce the regression coefficient to the 'not significant' level.

Examination of Fig. 1 shows that the macroporosity values tend to divide into two parallel groups according to their field classification, although evidence for terra rossas is scanty in the low porosity values. Since two families appeared to be present, regression lines were fitted separately to the two groups. These have coefficients which are not significantly different so that the two groups are represented by parallel regression lines. When the distance between regression lines is tested at the same value of free ferric oxide a significant difference is found at $P < 0{\cdot}01$.

Discussion

Stace (1956) and Norrish and Rogers (1956) have shown that the chemical and mineralogical properties of these two groups of soils are continuous from black to red and that any division is arbitrary. The significance of the distance between regressions of macroporosity on free ferric oxide content shows that the soils on which measurements have been made can be divided into two parallel groups on physical values. However, this does not mean that physical measurements provide a means of separating the two groups of soils, terra rossas and rendzinas. The profiles sampled were, in most cases, selected so as to avoid intermediates in such areas. If such a difference is general, it is difficult to see its use in field classification, as the physical difference measured in the laboratory is not always detectable in the field. Three profiles of each soil group have been examined in the field under equivalent moisture conditions; in these no difference in structure was apparent.

The pooled regression line in respect to the relation between macroporosity and free ferric oxide is interesting, considering the dominant role which is normally delegated to organic matter in structure formation. The value of total nitrogen corresponding to each value of free ferric oxide is given in Table 1. This value, as for free ferric oxide, is representative of the site rather than of the particular sample on which physical measurements were made. That a regression of such high significance can be obtained on free ferric oxide without considering organic matter would indicate that in these soils the main aggregating influence is the ferric oxide. This type of regression has been shown before by Lutz (1936), who measured aggregation at the 50 μ level of five different soils, and plotted this against free iron. In the terra rossa and rendzina soils it has been shown that chemistry and mineralogy are similar for both groups, and therefore more confidence can be placed in the regression value obtained here.

The role of free iron in aggregation is not understood. Its aggregating influence is ascribed to one or all of the following: (1) cementation due to precipitation of a hydrated iron gel and its irreversible dehydration (Lutz, 1936), (2) iron in solution preventing deflocculation (loc. cit.), (3) the formation of organic-mineral compounds of humic acids with free sesquioxides (Kvaratskhalia, 1951). At the pH values of these soils (Stace, 1956) it seems unlikely that any iron is in solution unless organic matter plays some role in bringing this about. An iron-organic matter complex seems possible, particularly in the light of work by Hua and

TABLE I

Total Nitrogen and Clay Content corresponding to Free Ferric Oxide (< 2 μ) Values plotted in Fig. 1

	Free Ferric Oxide, % of clay*	*Nitrogen,* % of soil*	*Clay < 2μ* % of soil*
Rendzinas .	1·0	0·28	35
	1·4	0·24	68
	1·5	0·20	75
	2·8	0·19	39
	3·1	0·38	34
	3·5	..	46
	5·3	0·29	51
	6·2	0·24	30
	6·2	0·19	43
	6·8	0·19	46
	8·5	0·33	33
	8·9	0·48	29
Terra Rossas	6·4	0·16	67
	9·4	0·15	67
	10·4	0·14	27
	11·3	0·14	47
	11·7	0·24	43
	12·2	0·15	60
	12·7	0·14	33
	14·0	0·31	30

* From Stace and Rogers (1954).

Samples for physical measurement were sometimes taken over depths equivalent to two chemical samples. In these cases average values of clay, nitrogen, and ferric oxide are given.

Chen (1945), who found that, in clay soils to which ferric hydroxide, organic matter, lime, and calcite were added, the iron compound had the greatest effect on aggregation, but that the binding effect was exerted only in the presence of organic matter. In the terra rossas and rendzinas sufficiently large quantities of organic matter for aggregation appear to be present even in those lowest in nitrogen, and it may be that the role of organic matter here is that suggested by Hua and Chen, iron being the limiting factor.

Summary

The macroporosity (air space at 100 cm. water tension) of soils which vary widely in free ferric oxide and organic matter has been measured. A highly significant regression of macroporosity on free ferric oxide has been obtained in spite of big variations in organic matter. The suggestion is made that the chief influence on the structure of these soils is the iron acting through the medium of an iron-organic matter complex.

The terra rossa and rendzina soils on which measurements were made may be represented by parallel regression lines, whose distance apart is significantly different from zero. Further evidence is necessary to show that this separation is of general application.

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THE HEAVY MINERALS OF SOME SOILS FROM THE NEIGHBOURHOOD OF CAMBRIDGE, ENGLAND

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Introduction

THE value of the 'heavy-mineral technique' as an aid to establishing the derivation of soils and soil parent materials has been recognized by many soil workers, for example in this country the studies of Hendrick and Newlands (1923, 1925), Hart (1929*a*, *b*), and Smithson (1953) may be mentioned. The method is particularly useful in areas covered by drift, where the relationship of soil to solid geology may often be obscured. The present investigation was carried out in an area extending about 18 miles to the north and north-east of Cambridge, in which the solid formations are diverse in character, and are overlain to a greater or lesser extent by a covering of glacial drift. The heavy minerals in the profiles of some representative soil series were studied, and their relative proportions ascertained to discover whether there are any significant differences between the mineral assemblages of the different soil series, and to find out, if possible, the origin of the sand fractions in these soils.

Geology. The geological strata represented are of the Jurassic and Cretaceous periods, with a covering in places of Pleistocene boulder clay and deposits of sand and gravel. The strike of the solid strata is from north-east to south-west and the dip is towards the south-east, so that the oldest formations such as the Kimmeridge Clay, the Lower Greensand, and the Gault occur in the north-west of the area (Fig. 1). The Corallian is represented by an isolated inlier of Oolitic Limestone and Coral Rag 3 miles long in a north–south direction and $\frac{3}{4}$ mile wide at Upware. The Gault occurs on both sides of the River Cam, and also forms a crescent-shaped ridge at Soham, partly enclosing Soham Mere in the north. In the south-east of the area is the Chalk represented by the Chalk Marl, the Grey Chalk, and the Middle Chalk, each of which is a progressively purer limestone than the formation below it.

The higher ground is covered by drift in many places, which on the Chalk is represented by the Chalky Boulder Clay, a yellowish brown sticky clay with numerous chalk fragments and flints. Elsewhere, on moderately high ground, patches of sand and gravel occur, now believed to be the remains of fans of material of glacial origin brought from higher ground by solifluxion. The large area of sand and gravel in the north-east forms the edge of the Brecklands, and is of glacial origin. The Fen deposits consist mainly of peat, overlying Fen clay or sandy alluvium.

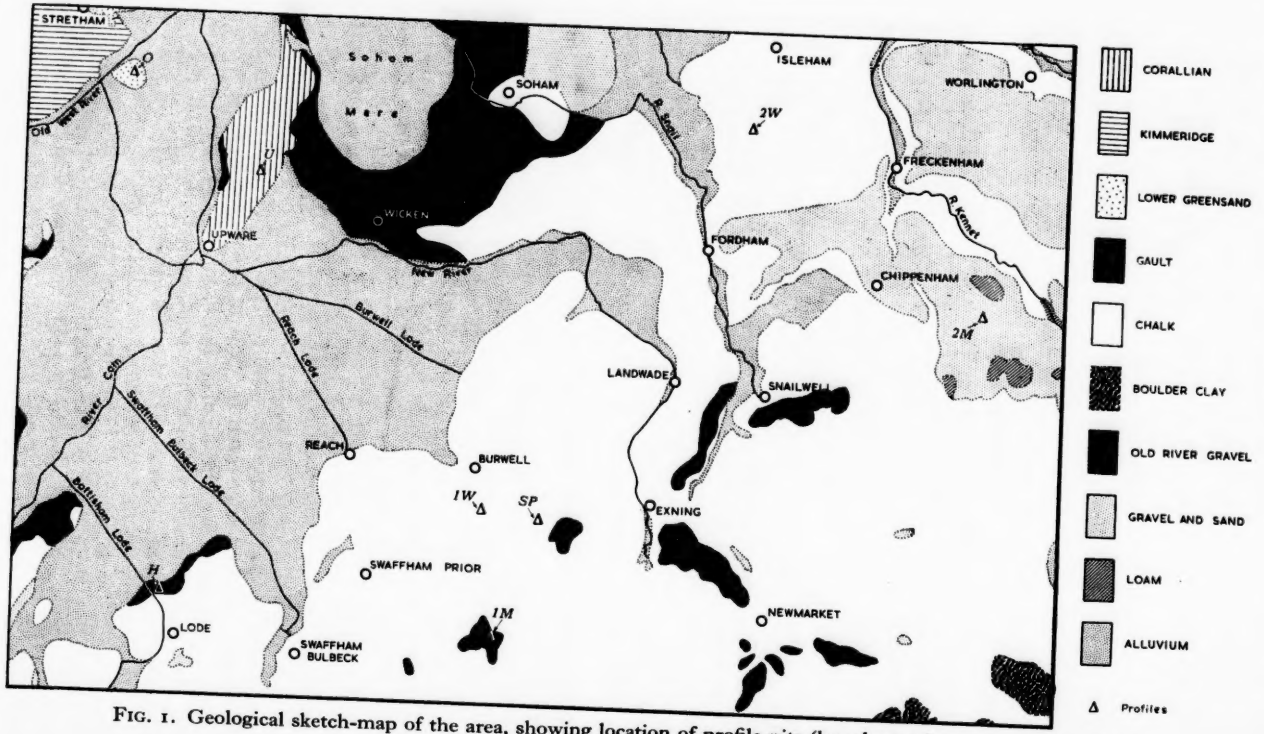

FIG. 1. Geological sketch-map of the area, showing location of profile pits (based on 1-in. maps, published by H.M. Geological Survey).

Soils

The soils of the area are extremely varied and profiles representative of six series were examined. The Moulton series is found on the well-drained sands and gravels which rest on Chalk. The Wantage series is a well-drained grey silty loam resting on Grey Chalk or Chalk Marl with only a little drift. Two profiles from each of these series were investigated. Intermediate in character between these two series is the Swaffham Prior series, in which the soils are similar to those of the Wantage except that there is a greater proportion of drift, though not so much as in the Moulton soils. The Highbridge series is an imperfectly drained heavy clay soil found over the Gault. The Corallian Limestone, with a certain amount of drift gives rise to the Upware series. The Oakington series is found on the Lower Greensand and is generally fairly well drained though rather heavy. One profile was investigated from each of these last four series. Detailed field descriptions of the profiles are given in the Appendix.

Experimental Procedure

About 50–100 g. of soil was treated with hydrogen peroxide to remove the organic matter, and the sand was separated by sedimentation, divided into a coarse (0·2–2 mm.) and a fine (0·02–0·2 mm.) fraction by sieving, and the heavy residues obtained by separation in bromoform. Before optical study it was necessary to clean the grains as most of them were heavily iron stained. Citric acid was first used as a cleaning agent, though it was later found that oxalic acid was more effective.

The relative amounts of the mineral species present in the separates of the fine sand fractions were determined by microscopic counts of between 300 and 600 grains for each sample, opaque grains other than ilmenite and magnetite being omitted. After computing the percentage composition, the results were expressed by allocating to each species a frequency number according to the method used by Evans, Hayman, and Majeed (1933): these data are presented in Table 1.

Distribution of the Minerals

In all the residues iron ores (ilmenite and magnetite) are the most abundant minerals. Zircon is fairly abundant, the grains differing greatly in degree of abrasion and there is some variation among the different samples, pink zircon, for example, being characteristic of the Lower Greensand. Garnet is very common and among those described many are characteristic of drift deposits: it is significant that the Oakington series, which is of Lower Greensand origin, shows a far smaller proportion of garnet than the other series. Minerals of the epidote group, tourmaline and amphiboles, are common in most of the samples though the latter is rare in the basal layer of the Oakington profile, which shows no marked signs of contamination with drift material. Probably most of the amphiboles were derived from drift: they are often blue-green in colour, which is characteristic of some of the

TABLE I

Relative Frequencies of the Heavy Minerals

Series	*Moulton*								*Wantage*				
Sample no.	*1M/1*	*1M/2*	*1M/3*	*1M/4*	*2M/1*	*2M/2*	*2M/3*	*2M/4*	*1W/1*	*1W/2*	*2W/1*	*2W/2*	*2W/3*
Minerals													
Zircon	6+	6+	6+	6	6+	6	6+	6	6−	6−	6	6+	6
Garnet	6	5	6−	6−	4	5	4	5	5	4	5	5	5
Kyanite	1	1	1	o	1	1	1•	1•	1	1	1•	o	1•
Staurolite	3	1	1	2	o	1•	1•	1•	1	o	1	o	3
Andalusite	1•	1•	o	1•	o	1•	o	1	o	o	o	1•	o
Sillimanite	1	o	1	1	1	1	2	o	1•	1	1	o	o
Tourmaline	4	4	4	2	3	4	3	4	4	3	4	5	5
Epidote group	5	4	5	5	6−	6−	5	6	5	5	6−	6−	5
Amphiboles	4	4	3	5	4	5	5	5	5	5	5	5	3
Pyroxenes	o	o	o	o	o	o	o	o	2	2	o	1	2
Biotite	o	o	o	o	o	o	o	o	o	o	o	o	o
Muscovite	o	o	o	o	o	o	1•	1•	o	o	o	o	o
Chlorite	o	o	o	o	o	o	o	o	o	o	o	o	o
Sphene	o	o	2	2	o	1	1	2	1	o	1	1	1
Anatase	o	2	o	o	4	3	2	3	3	1	3	2	2
Rutile	3	4	4	4	4	3	4	4	4	4	4	4	4
Brookite	o	1•	o	o	o	1	1•	1•	o	o	o	1	o
Ti-indet	3	2	4	3	4	4	5	4	2	2	o	2	2
Iron ore-ilmenite and magnetite	7	7	7	7−	7−	7−	6+	6	7	7+	7−	6	7

Series	*Swaffham Prior*		*Highbridge*					*Oakington*			*Upware*	
Sample no.	*SP/1*	*SP/2*	*H/1*	*H/2*	*H/3*	*H/4*	*H/5*	*O/1*	*O/2*	*O/3*	*U/1*	*U/2*
Minerals												
Zircon	6	6	6−	6−	6	6	6	6	6+	6	6	6+
Garnet	5	6	5	5	5	5	5	3	3	2	5	5
Kyanite	1	1•	2	1	1•	1•	1	4	3	4	1	1•
Staurolite	2	3	o	o	o	o	2	4	1	4	2	o
Andalusite	o	o	o	1	o	1	1•	o	1•	1•	o	o
Sillimanite	2	1•	o	o	1•	o	o	o	o	o	1•	1•
Tourmaline	5	5	4	4	4	5	5	4	3	4	4	4
Epidote group	4	5	6	6	6	5	5	3	5	3	6−	6−
Amphiboles	5	4	6−	5	5	5	5	4	4	1•	5	5
Pyroxenes	o	1	o	1•	o	o	o	o	o	o	o	o
Biotite	o	o	1	o	o	o	o	o	o	o	o	o
Muscovite	o	o	o	1•	o	o	1•	o	1•	o	o	o
Chlorite	o	o	o	o	o	o	o	o	o	1•	o	o
Sphene	2	1•	3	3	2	2	2	o	1	o	2	1
Anatase	1	1	3	2	2	2	2	o	2	1•	2	2
Rutile	4	5	4	4	5	4	4	4	4	5	5	5
Brookite	1•	o	1•	o	o	o	1•	o	o	o	1•	o
Ti-indet	3	3	4	5	4	5	4	2	5	4	4	5
Iron ore-ilmenite and magnetite	7	7	6−	6−	6	6	6+	7+	7	7+	6	6+

The ranges in percentages have been replaced by symbols as follows: 7+ = 45–59; 7 = 35–44; 7− = 28–34; 6+ = 23–27; 6 = 18–22; 6− = 14–17; 5 = 7–13; 4 = 4–6; 3 = 2–3; 2 = 1–2; 1 = ½–1; 1• = 1 grain only per slide; o = absent.

boulder-clay amphiboles. Pyroxenes, muscovite, and biotite are always rare.

Among the metamorphic minerals, kyanite is common in the profile of the Oakington series but is scarce in the other profiles. To a lesser extent the same applies to staurolite. Andalusite and sillimanite are rare in all the samples, though the former may occur in quite large grains in the coarse sand fractions.

Of the titanium minerals, rutile occurs commonly in all the samples, together with smaller quantities of anatase, sphene, and brookite. In addition, a number of shapeless semi-opaque grains were included as indeterminate titanium minerals, probably of secondary origin.

Phosphatic remains in the form of broken shells, &c., were found in the Wantage and Swaffham Prior profiles, but the figures for these were omitted as they could be broken very easily and were probably also dissolved to some extent in the acid treatment. Apatite might also have been dissolved.

Descriptions of the Minerals

Garnet

In the Moulton, Wantage, Swaffham Prior, and Highbridge profiles many different varieties occur, the grains being brownish or reddish orange, transparent-pink, or colourless. The orange-brown grains are

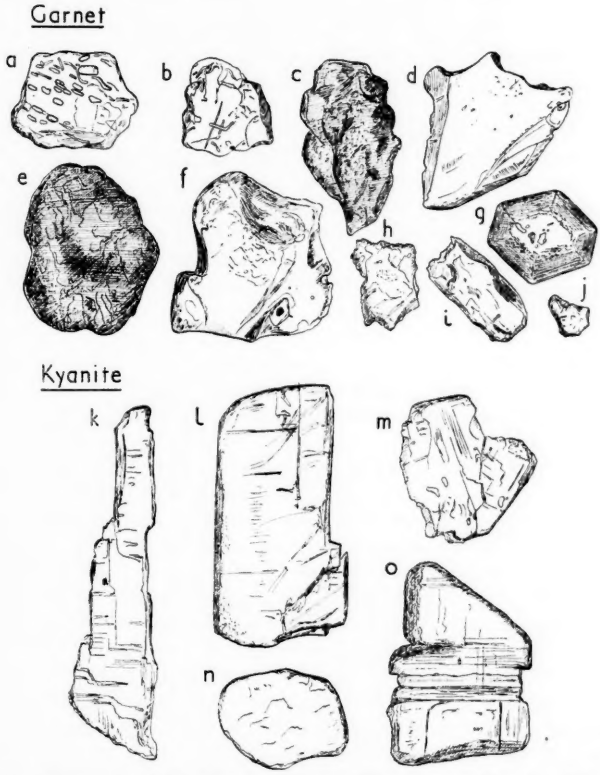

FIG. 2. *Garnet*: *a–d*, Moulton profiles; *e*, Wantage profile; *f*, *g*, Highbridge profile; *h–j*, Oakington profile. *Kyanite*: *k–m*, Oakington profile; *n*, Swaffham Prior profile; *o*, Moulton profile. Magnification: × 60.

generally very well rounded and usually contain a number of inclusions, especially of quartz: often they are full of dust-like particles, which give the grains a cloudy appearance and the surfaces are often pitted. Cloudy grains seem to be uncommon in the Wantage profile. The pink grains

are generally much clearer and contain fewer and smaller inclusions: though often well rounded, they sometimes show well-marked etching. Other grains are colourless and glass-like in appearance though it was found that even the clearest varieties showed at least some minute inclusions. The inclusions consist of colourless, often rather large, irregular particles apparently mainly of quartz. Rutile, especially as small prisms and needles, is also common (Fig. 2 *a* and *b*). Black iron ore sometimes occurs and occasionally tourmaline and some well-formed hexagonal flakes ascribed to biotite. Many inclusions appear to be cavities.

Most of the garnets in the Upware profile are small, having a glassy appearance and are transparent and angular with sharp jagged edges. The larger grains are generally more rounded and, the deeper coloured varieties especially, often contain more inclusions and are similar to those from the other profiles. A few of these almost colourless grains are etched so that prism-like steps and surface rhombs are formed.

In the Oakington samples garnets are less common than in the profiles described above, though there is a slight increase in amount from the lower to the upper layers as would be expected if the surface is contaminated with drift. They are generally colourless and irregular in outline like angular glassy chips (Fig. 2 *h–j*), and appear to differ from the types of garnet in the drift, though some pink grains similar to those described above occasionally occur in the upper layers of the profile.

Zircon

As can be seen from Table 1 the proportion of zircon is relatively constant from one profile to another, though each profile shows a considerable variety of forms.

Zircon is very variable in the Oakington profile which is derived from the Lower Greensand, being of all shapes from sharply angular grains to rounded ones. It varies in colour also, and though most grains are clear, some are cloudy, while many are pinkish or deep purplish (Fig. 3*c*): this last type is characteristic of the Lower Greensand (Rastall, 1919; Boswell, 1927). The well-formed crystals seem to be either four- or eight-sided prisms with usually bipyramidal terminations though some show simple pyramids. Among the inclusions are colourless crystalline minerals with relatively low refractive indices while some appeared to be iron ore. Other grains contain dust-like particles, which are probably more common among the coloured varieties. Zoned grains sometimes occur in this profile.

In the other profiles zircon occurs chiefly in rounded or subangular irregular chips and well-abraded prisms with pyramidal terminations. They are almost always colourless, generally water-clear, though some are rather cloudy due to dusty inclusions, which may cause the grains to appear yellowish or almost opaque: pink grains are very rare. Zoning sometimes occurs, but is not common. Colourless inclusions are fairly common and are prismatic, globular, acicular or streaky: they are generally irregularly arranged in the zircons though they may occasionally

be oriented parallel with the length of the crystal. Most of the colourless prismatic inclusions are probably quartz or apatite, while the globular ones appeared to be glass. Occasional inclusions are of biotite, rutile, iron ore, and minute dust-like particles.

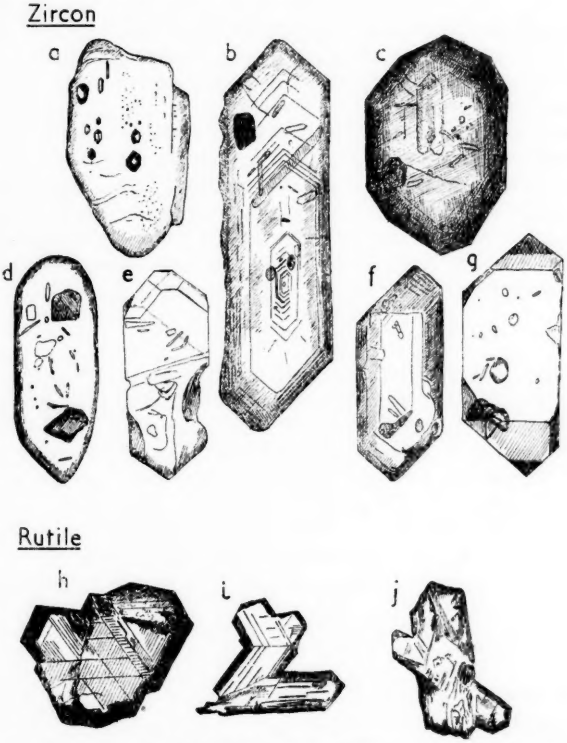

FIG. 3. *Zircon*: *a*, *b*, *d–f*, Moulton profiles; *c*, *g*, Oakington profile. *Rutile*: *h*, Oakington profile; *i*, Upware profile; *j*, Moulton profile. Magnification: × 220.

Kyanite

Kyanite is normally present only in small amounts, but is a common and characteristic mineral in the profile of the Oakington series, which might be expected as it is probably derived from the Neocomian formations and not from the glacial deposits.

In this profile the grains are generally over 0·15 mm. in size and range up to 0·8 mm. in length (Fig. 2 *k–m*). They are generally roughly rectangular, elongated parallel to (100) and show traces of the (010) and (001) cleavages, with the emergence of the acute bisectrix. One or two narrower grains show straight extinction through being parallel to (010). Most of the grains are rounded though some show re-entrant angles and jagged portions. Inclusions are not common.

All the other profiles contain grains of kyanite which are essentially similar in size and appearance though much rarer. They are generally fairly well rounded (Fig. 2*n*), though some are more subangular.

Staurolite

Staurolite is not common in any of the profiles though it is more frequent in the Oakington samples. In general it occurs in rounded or subangular grains, irregular in shape and orange-yellow in colour and showing marked pleochroism. The surfaces of the grains are very variable; often the ovoid grains have rough and pitted surfaces, while the irregular grains appear glassy or have a fractured conchoidal surface. Etched grains were sometimes seen, especially in the Highbridge profile, in which some of them also showed ragged ends. Some of the grains contain dusty inclusions in wisps and clots which may be quite frequent. Black inclusions attributed to iron ore are common, and some colourless inclusions of low refractive index may be gaseous or liquid.

Tourmaline

Tourmaline is common and usually appears as rounded flakes or abraded to angular prisms. Occasionally, as in the Highbridge profile, perfect hexagonal basal flakes occur. The commonest colour scheme is in shades of olive-brown or olive-green,* though reddish brown and occasional blue grains are present. The latter are rare, but are widespread and occur in most of the profiles, although they have not yet been recorded from the Swaffham Prior or the Oakington samples. Inclusions of varying sizes, but generally small, often occur as black opaque spots, which are probably iron ore, and as dust and colourless globules or prisms.

Rutile

Rutile is common though it varies considerably in form and size. It occurs generally as irregular grains and stumpy prisms of varying shades of yellow to orange-yellow, which are slightly pleochroic; some 'foxy-red', deep red, and grey grains also occur. Some of the rutile may be clear while other grains contain dark, possibly iron ore, inclusions. Twinning of both the geniculate and polysynthetic kinds occurs (Fig. 3 *h–j*).

Brookite

This is present in small quantities and generally occurs in small, often rather square, striated basal grains. The usual colour is clear, pale yellow, though occasionally the grains may be almost colourless. In appearance they are very similar to anatase, but can be easily distinguished by the varying polarization colours and anomalous interference figure.

* In some grains the colour is unevenly distributed, the centre sometimes being green and the outside olive-green-brown.

Anatase

Anatase generally occurs as flat, often square basal flakes with bevelled edges with varying degrees of abrasion. It is pale yellow to colourless and though often cloudy, is sometimes clear. The grains are usually small, though in the Oakington profile several were seen up to 0·2 mm. in diameter. Generally they show a certain amount of surface scratching so that they appear almost opaque.

Sphene

Sphene was found in small quantities, generally as well rounded but irregular, colourless to very pale yellow grains, the surfaces usually being fairly rough.

In addition to these recognizable minerals there are also a number of irregular yellowish grains often of a granular appearance, which have been included in Table 1 as indeterminate titanium oxide minerals. They are often almost opaque in parts, are generally fairly small and of about the same average size as the anatase and brookite.

Amphiboles

Amphiboles are fairly common occurring as ragged subangular or rounded flakes. They consist generally of the normal green hornblende, with pleochroism in various shades of olive-green. Blue-green flakes are also common and are probably arfvedsonite of Scandinavian origin, described by Rastall (1913) and Boswell (1916). A colourless amphibole with lower refractive indices also occurs. Inclusions are unimportant; some are colourless and some are iron ore.

Other minerals

Epidote is common, generally as rounded or irregular colourless or yellowish grains, usually fairly small, though occasionally larger grains occur. Many grains are colourless and of lower refractive index, though giving the characteristic straight compass-needle optic axis figure, and appear to be clinozoisite or zoisite, and sometimes show ultra-blue interference colours. Sillimanite and andalusite are fairly widespread, but scarce, as colourless irregular grains, the latter sometimes showing pale pink pleochroism. Pyroxenes are always rare but again are fairly widespread. They occur as greyish grains sometimes with the characteristic concertina-like ends and are possibly related to diopside. Biotite is present in the top layer of the Highbridge profile while muscovite appears to be more widespread though always rare. Chlorite also occasionally occurs. Apatite was occasionally seen though much of it was possibly destroyed by the acid treatment.

Conclusions

It has been found that the heavy mineral suites of most of the samples, except those of the Oakington series, are very similar, indicating that their sand fractions have a common origin, and are probably mainly derived from the glacial drifts with minor quantities of Neocomian material.

Among the diagnostic minerals indicating glacial drift is garnet, as has been stressed by earlier writers such as Rastall (1913), Boswell (1916), and Solomon (1932). In the drift it occurs as relatively large orange or transparent pink grains, the former often with numerous inclusions and the latter often etched. Greenish-blue hornblende is also characteristic of some of the drift deposits. The origin of the clay fractions has not been considered in this investigation, so that, although the heavy minerals of the Highbridge profile appear to indicate derivation from the drift, the sand is of minor importance compared with the clay which is probably mainly derived from the underlying Gault.

The profile of the Oakington series has a rather different composition which is probably due to the fact that the sand in it was derived largely from Neocomian sources and that contamination with glacial material is mainly confined to the surface layers. Kyanite, and to a lesser extent staurolite, is more prominent in this profile, and the large rectangular grains of the former appear to be characteristic of Neocomian sediments. Although zircon is common in both the drift and Neocomian deposits it has been found that pink zircons, such as occurs in this profile, are typical of the latter (Boswell, 1927).

The diversity of each mineral and the large numbers of different minerals in any sample are characteristic of the profiles. Counts were made to find the frequency of the heavy minerals in the fine sand fraction and it is concluded that counts taken of different fractions (for instance 0·2–1 mm. and 0·1–0·02 mm.) might show more significant differences, as the garnets derived from drift would tend to occur in the larger size fractions, while other minerals might be more prevalent in the smaller fractions.

Acknowledgements

The writer wishes to express his thanks to Dr. Stephen of Rothamsted Experimental Station, Harpenden, Professor Allen of Reading University, and Dr. Nockolds of Cambridge University who all gave their help and advice, and also Mr. Hodge of the Soil Survey and Mr. Pollok, formerly of the Soil Survey, both of whom gave valuable help in collecting and classifying the material.

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APPENDIX

Description of Profiles

Moulton series

Profile 1M. Collected at Gravel Pit Farm from near the top of a hill at an elevation of 140 ft. O.D. 1½ miles south-east of Swaffham Prior. Here the sands and gravels rest on the Middle Chalk and form one of the gravel patches representing an old river course which passes through Exning and Snailwell.

Sample 1.	0–6½ in.	Dark grey-brown sandy clay loam; a few small flints less than 1 in. in size.
„ 2.	6½–16 in.	Strong brown sandy clay loam; a few small flints.
„ 3.	16–22½ in.	As above, but more flinty.
„ 4.	22½–30 in.	Rounded chalk particles and loamy chalk, merging into hard chalk.

Profile 2M. Situated about 1 mile east of Chippenham on the sands and gravels of Breckland type, material most probably derived originally from the Boulder Clay.

Sample 1.	0–13 in.	Dark grey-brown sandy loam; occasional angular and sub-angular flints; non-calcareous.
„ 2.	13–18 in.	Brown loamy sand; many angular and subangular flints up to 1 in. in size; non-calcareous.
„ 3.	18–28 in.	Yellowish brown loamy sand; flints up to 2 in. in size; non-calcareous.
„ 4.	28–36 in.+	Very pale brown medium-textured sand with a few flints; patches of strong brown, coarse sandy clay loam; non-calcareous.

Wantage series

Profile 1W. Collected on the Grey Chalk about 1 mile south-south-east of Burwell. There is a very gentle slope in this locality and the elevation is 55 ft. O.D.

Sample 1.	0–8½ in.	Grey silty clay loam; occasional flints.
„ 2.	8½–13½ in.	Uniform slightly pinkish-grey silty clay loam; a few rounded chalk fragments.
„ 3.	13½–18 in.	Mainly white chalk with some material from above in the fissures.
	Below 18 in.	Solid chalk.

Profile 2W. Collected on low-lying land at an elevation of 25 ft. O.D. on Grey Chalk about 1 mile south of Isleham, and on the south side of the railway line.

Sample 1.	0–8 in.	Grey-brown clay loam with small white freshwater shells; highly calcareous.
„ 2.	8–17 in.	Pale brown clay loam with a few rounded chalk fragments; highly calcareous.
„ 3.	17–21 in.	White chalk rubble with yellow mottling.

Swaffham Prior series

Profile SP. Collected about 1 mile south-east of Burwell on the Grey Chalk. The ground is practically flat and at an elevation of about 80 ft. O.D. There is a certain amount of drift on the surface.

Sample 1.	0–9 in.	Grey-brown sandy clay loam; occasional flints.
,, 2.	9–20½ in.	Yellowish brown sandy clay loam; occasional flints.
	Below 20½ in.	Hard white chalk.

Highbridge series

Profile H. Collected on the Gault Clay on low-lying land at the edge of the Fens about 1 mile north-north-west of Lode Station. The elevation is about 15 ft. O.D. The clay appears to have been slightly contaminated with drift as a little sand occurs near the surface, and there are sandy patches in the immediate vicinity.

Sample 1.	0–8 in.	Very dark grey moderately organic loam with a few rounded subangular flints; strongly calcareous.
,, 2.	8–13 in.	Pale olive clay, heavily mottled with strong brown spots; there are a few small subangular flints and quartzite pebbles; weakly calcareous.
,, 3.	13–17 in.	Olive-grey clay, somewhat mottled with strong brown; occasional subangular flints; weakly calcareous.
,, 4.	17–18 in.	Strong brown clay with no stones; a few small iron concretions possibly of secondary origin; highly calcareous.
,, 5.	18–36 in.	Pale olive-grey clay mottled with pale yellowish brown; highly calcareous.

A few small lenticles of medium-grained sand occur.

Oakington series

Profile O. Situated about 1 mile south-east of Stretham on the Lower Greensand on a low knoll in the fens at an elevation of 5 ft. O.D.

Sample 1.	0–8½ in.	Uniform very dark grey-brown clay loam; very occasional flints; very slightly calcareous.
,, 2.	8½–23 in.	Mainly yellowish brown sandy clay loam slightly mottled with strong brown; some fragments of subangular ironstone at a depth of 18 in.; non-calcareous.
,, 3.	23–34 in.+	Uniform yellow-brown sandy clay loam; stoneless; non-calcareous.

Upware series

Profile U. Situated about 1 mile north-west of Wicken on the Corallian Limestone at an elevation of about 20 ft. O.D. in a slightly uneven field.

Sample 1.	0–8½ in.	Uniform grey-brown clay loam; occasional small flints; highly calcareous.
,, 2.	8½–15 in.	Uniform bright brown clay loam; occasional very small limestone fragments; highly calcareous.
	15–18 in.	Similar but with many limestone fragments.
	18 in.+	Moderately hard Corallian Limestone.

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THE ADSORPTION OF SUGARS BY MONTMORILLONITE
I. X-RAY STUDIES

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Summary

The adsorption of sugars by montmorillonite has been studied by X-ray diffraction methods. Complexes were found to be formed with a wide variety of sugars, each sugar forming complexes with one or two layers of molecules in each interlamellar region. For the one-layer complexes there was a close agreement between the interlamellar separation and the minimum molecular thicknesses of the sugar molecules determined from scale drawings. By comparison of the readiness of formation of the complexes under similar conditions, information about relative adsorption energies was obtained. Methylated sugars were found to be more strongly adsorbed than the other sugars examined, and sodium montmorillonite was found to yield two-layer complexes more readily than the clay with other exchangeable cations present.

Introduction

In the formation of the organo-mineral complex of soils the adsorption of organic matter by the clay components must take place in the presence of water. Very little is known at present about the adsorption of organic compounds by clay minerals in such circumstances, and the present work is aimed at throwing some light on this type of adsorption. Previous studies of the adsorption of fractions of soil-organic matter by clays have indicated that investigations of the adsorption of simpler organic compounds are very necessary if all the processes involved are to be understood.

The sugars and closely related compounds were selected for study in the present work as they form a well-defined chemical group known to complex with montmorillonite (Bradley, 1945) and related to the soil polysaccharides which are thought to be highly important in the formation of good soil structure (Martin, 1946; Geoghegan, 1950).

When Bradley (1945) observed the basal spacing of montmorillonite treated with aqueous solutions of various organic compounds to be characteristic of the organic compound he concluded that the compound was adsorbed in the interlamellar regions of the clay mineral to the exclusion of water. Later work (Glaeser, 1948; Mackenzie, 1948) has shown that this is only partially true, complexes with basal spacings characteristic of the organic compounds being obtained when both water and organic compound are present in the interlamellar regions. Nevertheless, by observing the effect of the adsorption of organic compounds on the basal spacing, it is possible to discover at least whether or not interlamellar adsorption is taking place, and if the number of adsorbed molecular layers in each interlamellar region can be determined then some idea of relative amounts of adsorption may be obtained.

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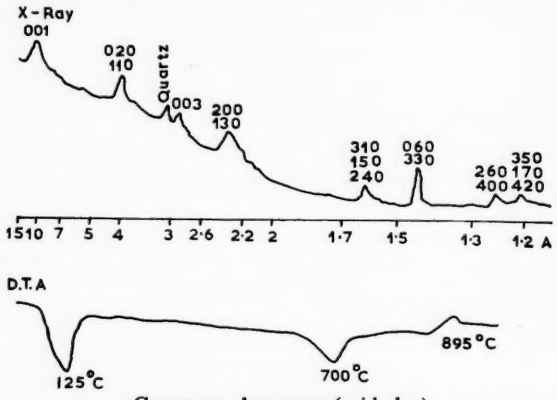
Materials

The montmorillonite was a commercial sample of Wyoming bentonite shown by X-ray diffraction, differential thermal and total chemical analysis to be uncontaminated except by *c.* 1 per cent. of quartz (Fig. 1). The acid clay was prepared by allowing *c.* 1 per cent. suspension of the



Chemical Analysis (acid clay)

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO/MgO	MnO	K_2O	Na_2O	H_2O+(300° C.)	H_2O-
54·75	0·11	19·36	3·38	0·19	0·15	0·10	0·33	13·38	7·86

Total—99·61

Fig. 1. Characterization of montmorillonite.

< 0·2 μ e.s.d. fraction of the natural material in 0·01 N ammonia to pass through a column of the hydrogen form of Amberlite IR 120. Sodium and potassium clays were obtained from the acid clay by neutralization with the appropriate base. Calcium and magnesium clays were prepared by leaching with solutions of the appropriate chlorides and removing excess chloride by water-washing. The cation-exchange capacity of the natural material at pH 7 was 82 m.e./100 g. The sugars were kindly supplied by Dr. R. B. Duff of the Soil Organic Matter section of the Macaulay Institute for Soil Research. They had all been shown by standard chemical methods to be very pure.

Method

The X-ray camera was an evacuated 9-cm. powder camera of the type described by MacEwan (1946) used with CoK α radiation. The films were measured with a Hilger film measuring rule, relative intensities of lines being estimated visually. Direct X-ray examinations of 4 per cent. suspensions of air-dry montmorillonite in sugar solutions of different strengths sealed into fine glass capillaries failed for sodium, potassium, and the acid montmorillonite to reveal any basal reflections; for calcium and magnesium montmorillonite basal reflections at 19·3 Å were observed, but this spacing was unaffected by varying the sugar concentration from 0 to 50 per cent. However, when clay-sugar aggregates prepared by

evaporation from the suspensions were examined the basal spacings were found to be characteristic of the sugar even when the complexes were formed from solutions of initially only 1 per cent. concentration. This evaporation aggregate technique was therefore used for all X-ray examinations to be described.

Results

Each sugar examined was found to form complexes with two, and in a few cases three, different basal spacings. The observed spacings of the complexes formed by any one sugar were dependent only on the sugar,

TABLE 1

Effect of Initial Sugar Concentration on Formation of Ca-*montmorillonite-sugar Complexes*

Sugar	*Montmorillonite concentration, %*	*Sugar concentration, %*	*d*(001)*Å*	*Type of complex*	*Ratio of types*
(*a*) *At constant montmorillonite concentration*					
Glucose	5	5	18·1	2-layer	..
„	5	2·5	14·5	1-layer	..
„	5	1	14·6	1-layer	..
Xylose	2·5	2	20·6 14·4	2- and 1-layer	1:3
„	2·5	1	14·1	1-layer	..
Lactose	2·5	1	18·2 14·4	2- and 1-layer	4:1
„	2·5	0·5	14·4 12·2	1- and 0-layer	2:1
(*b*) *At constant montmorillonite : sugar ratio*					
Xylose	2·5	2	20·6 14·4	2- and 1-layer	1:3
„	1·25	1	19·6 14·0	2- and 1-layer	1:5
Mannitol	2·5	2	16·6 14·4	1½- and 1-layer	1:3
„	1·25	1	14·0	1-layer	..
Sucrose	2·5	1	16·5	1½-layer	..
„	1·25	0·5	15·9d*	1½- and 1-layer	1:1
Cellobiose	2·5	1	18·4 14·4	2- and 1-layer	3:2
„	1·25	0·5	14·3	1-layer	..

* d = diffuse.

but the sugar concentration and exchangeable cation effected the relative proportions of the different complexes found in a single aggregate. Generally, when more than one complex occurred in a single aggregate two sets of basal spacings were observed, each set corresponding to one complex. The aggregate must therefore have contained separate 'domains' of each type, as random interstratification would produce diffuse reflections corresponding to intermediate spacings and regular interstratification a single series of orders of a higher spacing (MacEwan, 1949).

Low-angle reflections which were occasionally observed corresponding to spacings greater than 25 Å are probably due to reflections from a system formed by the interstratification of domains. Although the great majority of reflections observed were clear and sharp, occasional diffuse lines appeared, notably when an aggregate contained a 'zero-layer complex', i.e. when some interlamellar regions contained no sugar molecules at all.

TABLE 2

Effect of Exchangeable Cation on Formation of Montmorillonite-sugar Complexes

Exchangeable cation	*Sugar*	*Montmorillonite concentration, %*	*Sugar concentration, %*	*d(001)Å*	*Types of complex*	*Ratio of types*
H	Glucose	5	2·5	18·5	2-layer	..
Na	,,	5	2·5	18·1	2-layer	..
K	,,	5	2·5	14·3	1-layer	..
Ca	,,	5	2·5	14·5	1-layer	..
H	,,	2·5	1	14·0 12·2	1- and 0-layer	2:1
Na	,,	2·5	1	18·5	2-layer	..
K	,,	2·5	1	13·3d*	1- and 0-layer	2:1
Ca	,,	2·5	1	14·2 12·1	1- and 0-layer	2:1
Mg	,,	2·5	1	17·9 14·3	2- and 1-layer	1:2
Na	Mannose	3	1·5	19·2 15·9	2- and 1-layer	1:2
Ca	,,	5	2·5	16·0	1-layer	..
Na	Sucrose	3	1·5	19·5 16·4	2- and 1½-layer	3:2
Ca	,,	2·5	1	16·5	1½-layer	..
Na	Galacturono-lactone	3	1·5	18·0	2-layer	..
Ca	,,	4	2	17·5 15·2	2- and 1-layer	1:1

* d = diffuse.

Previous studies of interlamellar adsorption by montmorillonite have indicated that the adsorbed molecules are taken up in discrete layers. The correlation of the observed basal spacings of the sugar complexes with the molecular structures of the sugar molecules, to be discussed below, makes it clear that the same type of 'layered' adsorption occurs here. In Tables 1, 2, and 3 estimates are given of the relative amounts of each type of complex (one- or two-layer) for any aggregate containing more than one. It is assumed that equal quantities of each type lead to two sets of reflections with equally strong first orders, and that the intensities of the higher orders relative to the first vary in the same way as in an aggregate containing only one type of complex.

Tables 1 and 2 show that both sugar concentration and the exchangeable cation affect the adsorption. Hence to compare the adsorption of

different sugars it is obvious that the complexes should be prepared under exactly similar conditions. The technique adopted was to prepare the aggregates from a 2·5 per cent. suspension of calcium-montmorillonite in

TABLE 3

Sugars and Related Compounds in Decreasing Order of Adsorption Energies on Montmorillonite with Δ-values and Minimum Molecular Thicknesses determined from Scale Drawings

Sugar	Δ-value, Å		Minimum molecular thicknesses, Å
	1-layer	2-layer	
1. 2:4:6 trimethyl glucose	5·1	9·2	5·3
2. 4:6 dimethyl glucose	5·6	10·9	5·3
3. Arabinose	..	9·0	..
4. Ascorbic acid	..	8·3	..
5. Fucose	..	9·4	..
6. N-acetylglucosamine	..	8·1 (& 10?)	..
7. Cellobiose	5·0	8·8	5·1
8. Lactose	4·8	8·7	5·3
9. Maltose	5·4	9·3	5·4
10. Melibiose	5·3	8·8	5·3
11. Galacturonolactone	5·8	8·5	..
12. Raffinose	5·8	9·1	..
13. Rhamnose	6·4	12·8	5·9
14. Sucrose	5·6	9·1	5·6
15. α-methyl glucoside	5·8	..	5·7
16. Sorbose	5·3	..	5·2
17. Erythritol	5·2	9·1	..
18. Galactose	5·8 / 5·0	..	5·3
19. Heptulose	6·2	..	..
20. i-inositol	4·9	..	..
21. Xylose	4·7 / 5·1	9·6	4·8 / 5·2
22. Glucose	4·8 / 5·2	9·3	4·7 / 5·3
23. Mannose	6·7	10·4	5·9
24. Mannitol	5·0 (and 6·8?)	..	..
25. Gluconolactone	5·7	..	..
26. Glucuronolactone	5·7	..	..
27. Glucosamine	4·8	..	4·7 / 5·3

a 1 per cent. solution of the sugar. As the preparation of a single aggregate did not distinguish between the readiness of adsorption of all of the sugars examined, some results are included in Table 3 for complexes prepared under other conditions. In this way one-layer Δ-values for some of the strongly adsorbed sugars and two-layer Δ-values for some of the weakly adsorbed ones were obtained. It has been attempted to arrange the sugars in order of decreasing adsorption energies, assuming that those sugars which form a two-layer complex from the more dilute solutions have the highest adsorption energies and that those sugars which require high initial sugar concentrations to form a complex have low adsorption energies. In Table 3 the Δ-value is given instead of the basal spacing so

that a direct comparison may be made with the minimum molecular thicknesses of the sugar molecules. (The Δ-value is equal to the observed basal spacing less 9·4 Å, the distance between the outer surfaces of the outer oxygen sheets in each alumino-silicate lamella (MacEwan, 1948)).

Discussion

Correlation of Δ-values with molecular structures

Although the chemical structures of the sugars are mostly well established, the only sugars whose exact molecular dimensions have been determined in detail from X-ray crystal analyses are glucose (McDonald

TABLE 4

Δ-values of Montmorillonite-Glucose Complexes

Exchangeable cation	*Initial clay concentration, %*	*Initial sugar concentration, %*	*Δ-value, Å*	*Minimum molecular thickness, Å*
Ca . .	2·5	1	5·3	
Ca . .	2·5	1	5·4	α-glucopyranose 5·3
Ca . .	2·5	1	4·8*	β-glucopyranose 4·7
Ca . .	5	2·5	5·2	
Ca . .	5	1	5·2	α-glucofuranose 4·7
K . .	5	2·5	4·6	β-glucofuranose 4·7
H . .	2·5	1	4·5*	
Mg . .	2·5	1	4·9†	straight chain 4·6
K . .	2·5	1	4·6*	
Na . .	3·5	1	4·8†	

* With zero-layer complex in aggregate.
† With two-layer complex in aggregate.

and Beevers, 1952), sucrose (Beevers and Cochran, 1947; Beevers *et al.*, 1952), and ribose in cytidine (Furberg, 1950). However, by assuming that the dimensions of the pyranose and furanose rings found in the crystals of these sugars persisted in the others, and by making the necessary adjustments of the chemical groups around the rings, scale drawings of all the sugars were prepared. Van der Waals radii were taken from Pauling (1950) and hydrogen was given the value 1·2 Å. Some of these drawings showing the minimum molecular thickness are reproduced in Fig. 2. For the sake of clarity the carbon-oxygen ring is shown slightly tilted from its actual position and hydrogen atoms of hydroxyl groups are omitted except where they contribute to the minimum thickness. The $-CH_2OH$ group which is free to rotate has been shown in a position where it does not contribute to the thickness; for the disaccharides it has been omitted from the drawings. The mimimum thicknesses for both α- and β- forms of both pyranose and furanose rings were determined.

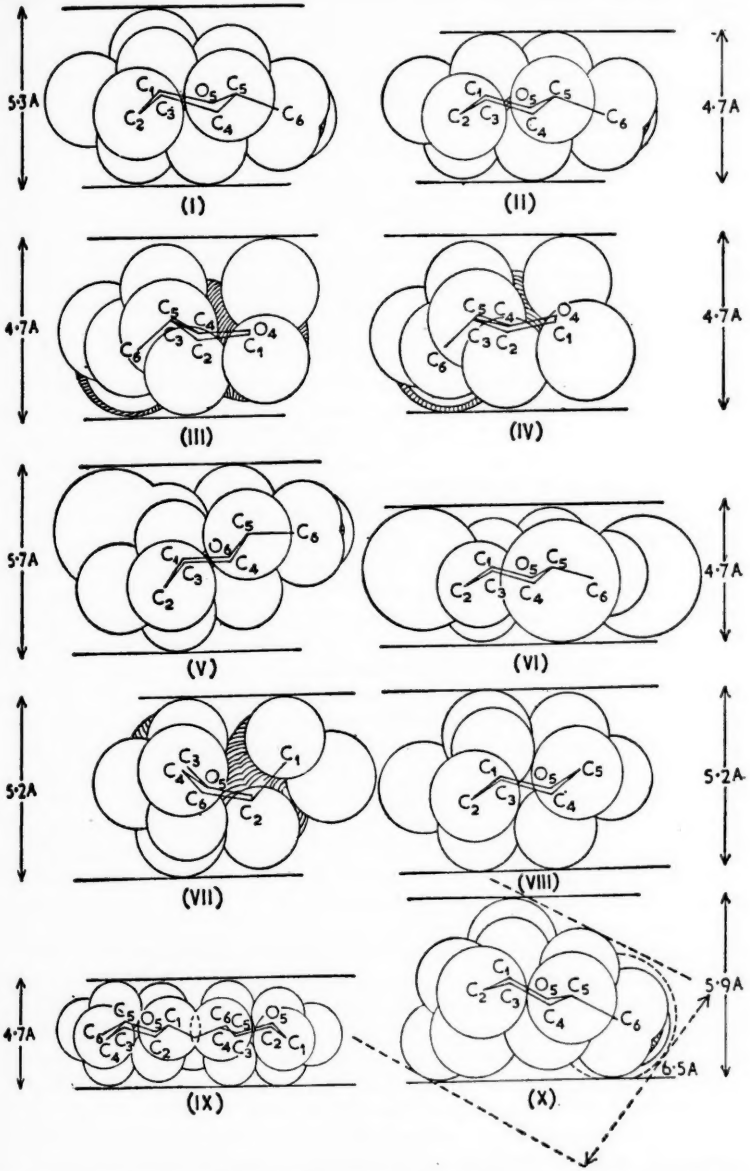


FIG. 2. Minimum molecular thicknesses of sugar molecules. (i) α-glucopyranose, (ii) β-glucopyranose, (iii) α-glucofuranose, (iv) β-glucofuranose, (v) α-methyl glucoside, (vi) 2:4:6:trimethyl-β-glucose, (vii) α-sorbofuranose, (viii) α-xylopyranose, (ix) β-cellobiose, (x) α-mannose (and rhamnose).

It is clear from the results in Table 3 that the Δ-value and minimum molecular thickness for most of the sugars examined are in good agreement. It is particularly striking that when two slightly different basal spacings have been observed they can be directly related to the α- and β- forms of the sugar. This is illustrated by the results for glucose collected in Table 4. The very close correlation of the basal spacing of the α-methyl glucoside complex and the minimum thickness of the molecule should also be noted. It thus seems certain that the smallest observed spacing for any complex corresponds to the adsorption of a single layer of sugar molecules in each interlamellar region, the sugar molecules lying as flat as possible between the oxygen sheets of the adjacent aluminosilicate layers. This is what would be expected from the results of Hendricks (1941) and Talibudeen (1955) for protein adsorption by montmorillonite, and those of MacEwan (1948) for the adsorption of various very simple organic compounds.

The slight differences observed between Δ-value and minimum molecular thickness may be attributed to various causes: uncertainty about the exact dimensions of the sugar molecules; the effect of adsorption on those dimensions; the uncertain Van der Waals radius of the hydrogen atom; the effects of small amounts of random interstratification in the complexes; and the effect of water molecules retained with the sugars in the interlamellar regions.

Two sugars, rhamnose and 4:6 dimethyl glucose, have second Δ-values exactly twice those of the single-layer complexes. For most of the sugars examined, however, the second Δ-value was equal to rather less than twice the first. It is concluded that the second value represents the adsorption of two layers in each interlamellar region, with some interpenetration of the adsorbed layers. An intricate network of hydrogen bonds is known to be formed in the sugar crystals (Beevers and Cochran, 1947; McDonald and Beevers, 1952) and so this interpenetration is quite probable. Further, Bradley (1945) observed the 18·3-Å spacing of the sucrose complex and constructed a two-dimensional Fourier curve from his X-ray data. Unlike the Fourier curves for the two-layer complexes with very simple organic molecules, this showed no distinct peaks in the interlamellar region, but a single very broad peak, consistent with the hypothesis that the layers interpenetrate. A similar interpenetration of the adsorbed layers has been observed by Talibudeen (1955) when studying double-layer montmorillonite-protein complexes.

The possibility that sugar molecules are arranged in the interlamellar spaces in some less simple manner cannot, however, be entirely ruled out. Where intermediate spacings have been observed it seems probable that these are due to some alternative packing of the molecules, e.g. for sucrose the intermediate 16·5-Å spacing is probably produced by a different orientation of the glucose and fructose portions of the sucrose molecule with respect to each other, compared with the arrangement giving the minimum molecular thickness, and an arrangement of the mannose and rhamnose molecules which gives a much closer agreement with the observed Δ-values is indicated in Fig. 2.

Unless the H-atoms of the hydroxyl groups project from the general

plane of the molecule there is no indication of an approach to the alumino-silicate surface closer than corresponds to Van der Waals contact, in contrast to the findings of Greene-Kelly (1955) for aromatic molecules adsorbed by montmorillonite. Also the second Δ-values appear to be too small to be due to an arrangement where the planes of the adsorbed molecules are at right angles to the alumino-silicate surface, again in contrast to what was observed with complexes of aromatic molecules. The close similarity of the single layer Δ-values of β-glucose, 2:4:6 trimethyl-β-glucose and cellobiose, 4-(β-glucopyranosido-) glucopyranose, 4·7, 5·1, and 4·9 Å respectively, is very strong evidence for the flat configuration of the adsorbed molecules, as the minimum molecular thicknesses of these three molecules are similar, but their other dimensions differ very considerably.

The effect of sugar concentration on the adsorption

Table 1 shows that the proportion of the two-layer to the one-layer complex increases as the sugar concentration increases in accordance with the general rule for physical adsorption. The maximum amount of adsorption does not appear to exceed that represented by the formation of a two-layer complex. This was so, even when the complex was prepared from a 20 per cent. solution of a very strongly adsorbed methylated glucose. For concentrations of less than 1 per cent. no indication of the formation of complexes appeared except for the methylated glucose and glucosamine. Thus it appears that adsorption starts with solutions of about 1 per cent. concentration and reaches a maximum at about 4 per cent. It must, however, be remembered that the aggregates examined were prepared by evaporation from the solutions and that during the evaporation the sugar concentration would have risen. Adsorption most probably took place during the evaporation, and the initial concentration serves only as an index of the time during which the concentration of sugar exceeded the point where adsorption commenced. No accurate estimate of the quantitative amount of adsorption can be made from these observations because the interlamellar regions almost certainly contained water as well as sugar molecules, as was shown by Mackenzie (1948) and Glaeser (1948) for other montmorillonite-organic complexes.

The effect of the exchangeable cation on the adsorption

From Table 2 it is evident that the amount of adsorption for a given sugar from a solution of given concentration varies with the exchangeable cation in the order $K < Ca < Mg < H < Na$. The effect of the exchangeable cation on the expansion of previously dehydrated montmorillonite when treated with organic compounds has been found to be $K < Na < Ca < H < Mg$ (Barshad, 1952). The orders are similar except for the position of sodium and it is reasonable to assume that the difference is associated with the high dispersion of the sodium-saturated clay. (It is of course possible that the sugars themselves affect the dispersion of the clay mineral, but the direct X-ray examination of suspensions of the clay in sugar solutions gave no indication of this.) When the

adsorption of sugars occurs from aqueous solution the ease of entry of the organic molecules into the interlamellar positions will be affected both by the dispersion of the clay mineral as well as by any direct attraction between exchangeable cation and organic molecule. With sodium as exchangeable cation the clay mineral is completely dispersed in aqueous suspension (Schofield, 1947; Norrish, 1954) so that there is no necessity for the organic molecules to actually penetrate the interlamellar regions.

The effect of the nature of the sugar

All the wide range of compounds examined gave definite evidence of interlamellar adsorption, but there were striking differences in the sugar concentrations required to give one- or two-layer complexes. A consideration of the results in Table 3 allows the following generalizations to be made; methylated glucoses are very strongly adsorbed, much more so than unsubstituted sugars; carboxyl or amino-substituted glucoses are physically less strongly adsorbed than the unsubstituted sugar; disaccharides are more strongly adsorbed than monosaccharides.

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THE ADSORPTION OF SUGARS BY MONTMORILLONITE
II. CHEMICAL STUDIES

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Summary

The effect of methoxyl, amino, and carboxyl groups on the adsorption of sugars by montmorillonite has been examined by simple chemical methods. The strong adsorption of methylated sugars has been confirmed. Mechanisms by which the adsorptions of these substituted sugars may take place are suggested. It is considered that these mechanisms contributed to the observed large adsorption of a soil polysaccharide.

DURING an X-ray diffraction study of the adsorption of sugars by montmorillonite (Greenland, 1956) certain substituent groups in the sugar nuclei were found to affect the adsorption considerably. A further study of the influence of these substituents has now been made, the adsorption being followed by chemical methods. In the present paper mechanisms of adsorption are suggested, and the possible importance of these in soils discussed.

Materials

The sample of montmorillonite used and the methods by which it was saturated with different exchangeable cations have been previously described (Greenland, 1956). The sugars had all been shown by standard chemical methods to be very pure, except the sample described as 'a methylated glucose'. This contained the methyl glycosides of di-, tri-, and tetra-methyl glucose in the proportions 1:4:5 (estimated chromatographically). The soil polysaccharide was a sample that had been separated and purified according to the technique described by Forsyth (1947).

Experimental

The apparent adsorption of the sugars was determined by shaking a solution of known strength with the clay mineral and measuring the change in concentration of the supernatant liquid. To correct the apparent adsorption for solvent adsorption it was assumed that the necessary correction was that just sufficient to make the adsorption positive and increase continuously with initial sugar concentration. It was further assumed that the total amount of solvent adsorption was independent of the initial sugar concentration.

The fixation of sugar was determined by washing the sugar-clay complex with distilled water until no further reduction occurred in the carbon content of the complex.

For determinations by both methods suspensions of the clay mineral were prepared in sugar solutions of accurately known strength. After shaking overnight the suspensions were centrifuged in tubes sealed to

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prevent evaporation of the solution, and aliquots of the supernatant liquid removed. The sugar content of each aliquot was then determined by a wet oxidation method (Walkley and Black, 1934). This method was found to give results consistent to 0·5 per cent. applicable over a wide range of concentrations and to a variety of sugars. For greatest accuracy

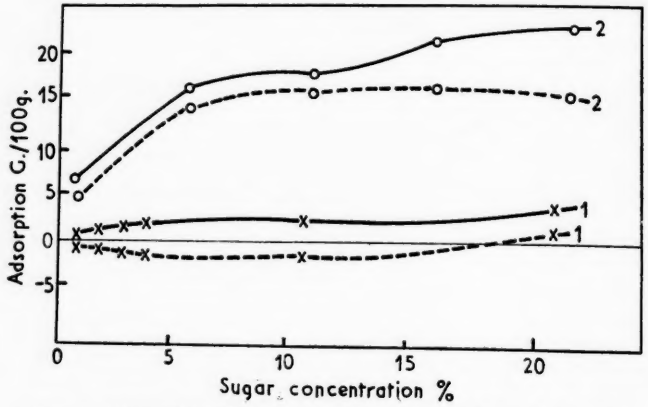

FIG. 1. Adsorption of glucose (curves 1) and methylated glucose (curves 2) by Mg-montmorillonite. (Full lines, corrected adsorption; broken lines, apparent adsorption.)

it was essential to determine the oxidation factor for each sugar at each concentration used (the factor was found to vary from 97 to 99·5 per cent., but was very consistent for specified conditions). To determine the fixed sugar samples were allowed to air-dry after the water washings and carbon determined by combustion analysis. All results were expressed in terms of clay dried to constant weight at 300° C. When adsorptions were determined at various pHs the suspensions were prepared with hydrogen or calcium clays and different amounts of distilled water and diluted calcium hydroxide added. The pHs were read on a Muirhead pH meter with glass electrode, after the suspensions had been shaken overnight.

Discussion

The most surprising observation made during the X-ray examination of sugar adsorption by montmorillonite was that methylated sugars were much more strongly adsorbed than simple sugars or sugars with other substituents present. Comparison of the curves obtained for the variation in adsorption of glucose and methylated glucose with sugar concentration (Fig. 1) shows that this is fully confirmed by the chemical results. Hydrogen bonds would be expected to be formed between sugar and clay just as between water and clay (Hendricks and Jefferson, 1938; Mathieson and Walker, 1954) or alcohols and clay (Bradley, 1945). Methylation of the sugar would be expected to decrease the adsorption, as the hydroxyl groups which presumably participate in hydrogen bond

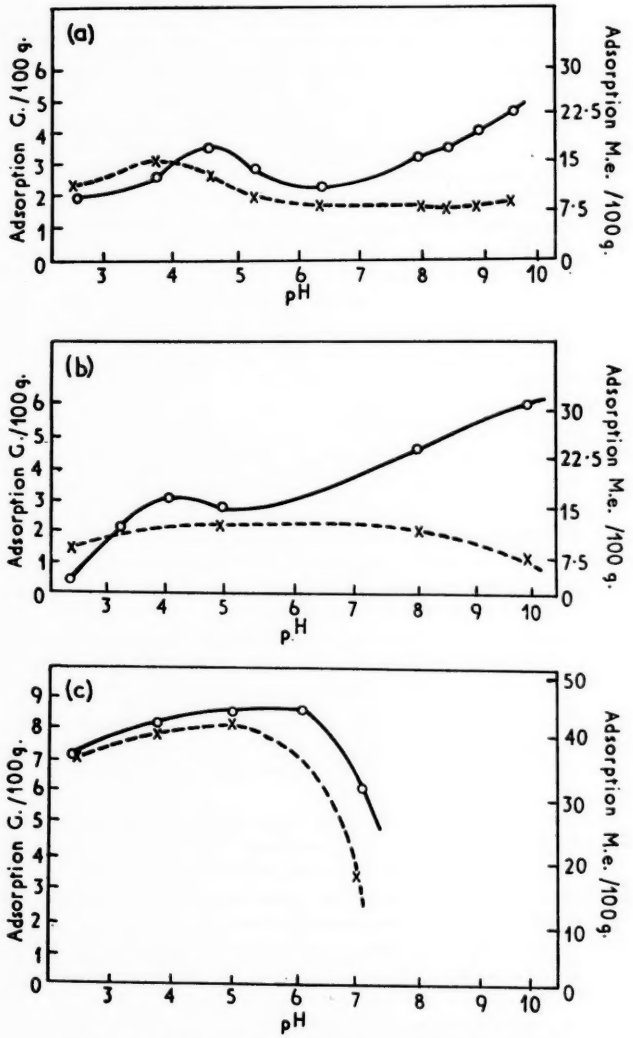

FIG. 2. Variation of adsorption with pH (*a*) of glucuronic acid, (*b*) of gluconic acid, (*c*) of glucosamine. Full lines, corrected adsorption; broken lines, fixation. 4% sugar solutions in 4% H-Ca-montmorillonite suspensions.

formation are replaced by methoxyls. The most likely explanation of why the adsorption is in fact enhanced rather than decreased would seem to be that hydrogen bond formation involving partially negatively charged oxygen atoms such as exist on the interlamellar surfaces of montmorillonite is stronger to carbon atoms than to other oxygens. The carbon atoms of methoxyl groups are more electro-positive than the oxygens of the corresponding hydroxyl groups, so that a tendency of the methoxyl groups to neutralize the surface charge of the clay may contribute to the adsorption energy. A further contributory factor may be the tendency of methylated sugars to form polymerized molecules (Bell and Northcote, 1950). Although there is only slight evidence that such polymers are formed in aqueous solution, it is possible that the attraction between the adsorbed molecules can come into play when the molecules are closely juxtaposed as on the clay surface.

The effect of introducing amino or carboxyl groups into the sugar nucleus was much less marked than the effect of methoxyls. However, the chemical results for the adsorption of these compounds show that an interesting variation with pH occurs (Fig. 2). A maximum in the adsorption of both sugar amine and acids is observed at about pH 4–5. At this pH adsorption and 'fixation' of the sugar are equivalent and so a chemical adsorption mechanism must operate. For the amine this is obviously the adsorption of the cationic form of the sugar on the permanent negative spots of the clay. For the sugar acids it is most probably due to the adsorption of sugar anions on the positive spots which occur on the edges of the clay lattice at acid pHs (Schofield and Samson, 1953, 1954; Emerson, 1954). For the sugar acids an increase in adsorption at pHs greater than 7 was observed. It is interesting to note how closely this behaviour parallels that of phosphate ions shaken with montmorillonite suspensions (Goldsztaub, Henin, and Wey, 1954). Here the maximum in the adsorption curve at pH 4–5 is explained as due to complex formation with iron and aluminium ions. However, on the evidence at present available it is impossible to decide whether this mechanism or adsorption on positive spots is what actually occurs. It is possible that both contribute.

The increasing adsorption of the sugar acids as the pH rises above 7 is probably to be explained, as is the adsorption of phosphate at high pH, by the precipitation of insoluble salts of the acids. The precipitation must, however, be partly due to the influence of the clay mineral, as the sugar acid was found to dissolve readily in calcium hydroxide solutions to form solutions of the same pH and concentration as would occur in the clay suspensions if no precipitation occurred. It may be that the adsorption at high pH takes place through bridge linkages, the divalent calcium cations linking negatively charged sugar anions to negatively charged clay particles. Such linkages would be expected to become commoner as the concentration of the calcium ion increases.

Soil polysaccharides have been shown to contain simple sugars and sugar acids (Forsyth, 1950), sugar amines (Bremner, 1950), and methylated sugars (Duff, 1952). Thus the adsorption of soil polysaccharides by clays can occur through any or all of the mechanisms so far discussed,

and may involve both interlamellar and external surfaces of the clay mineral particles. It is thus not surprising to find that a soil polysaccharide is very strongly adsorbed and fixed by montmorillonite (Table 1). It is

TABLE 1

Adsorption of Glucose, Methylated Glucose, and a Soil Polysaccharide by Magnesium Montmorillonite

(1 per cent. solutions in a 4 per cent. clay suspension)

	Glucose	*Methylated glucose*	*Soil polysaccharide*
Adsorption .	2·1	4·2	13·9
Fixation .	1·0	1·8	8·9

In g./100 g. dry clay.

interesting to note that the magnitude of the adsorption is considerably greater than the adsorptions of fulvic and humic acids that have previously been reported (Jung, 1943; Khan, 1950; 1951). The maximum adsorptions found by these authors, using suspensions of initially rather higher clay:organic matter ratio, did not exceed 2 g. per 100 g. clay.

TABLE 2

Basal Spacings of Calcium Montmorillonite-Soil Polysaccharide Complexes

(From X-ray diffraction diagrams of oriented aggregates prepared by evaporation from 4 per cent. clay suspensions)

Polysaccharide concentration, %	*d*(001) Å
1 . . .	14·6
4 . . .	14·6
10 . . .	16–18

Jung (1943) failed to obtain any evidence of interlamellar adsorption of his organic matter fractions, but it is clear from the results of an X-ray examination of the soil polysaccharide-montmorillonite complex (Table 2) that interlamellar adsorption does take place here (for details of the X-ray techniques employed see Greenland, 1956). The suggestion may thus be tentatively made that the soil polysaccharides are preferentially adsorbed to other constituents of soil-organic matter.

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